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Document Subject

TRANSMITTAL OF "THE WORK PLAN TO EVALUATE THE BEHAVIOR OF BURIED CONCRETE AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE " (RF/RMRS-98-279-UN) - JEL-166-98

KH-00003NS1A October 8, 1998

Discussion and/or Comments

Attached are two (2) uncontrolled copies of the ***Work Plan to Evaluate the Behavior of Buried Concrete at the Rocky Flats Environmental Technology Site*** as submitted by British Nuclear Fuels, Limited Comments from the last review have been incorporated These copies are for information only since this document has not been controlled and will need to be controlled prior to performing work There are still some outstanding based on the response to Quality Assurance comments These issues will need to be further addressed in this document or more likely, in the quality assurance plan/sampling and analysis plan yet to be prepared

If you have any questions regarding this document please contact Craig Cowdery at extension 2055

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A Work Plan to Evaluate the Behavior of Buried Contaminated Concrete at The Rocky Flats Environmental Technology Site

Submitted to

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RMRS
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Contents

1. Executive Summary

This report describes a draft work plan to examine the environmental behavior of plutonium, americium and uranium present as a contaminant on the surface of construction concrete at the Rocky Flats Environmental Technology Site (RFETS) Following decommissioning activities at RFETS around 120,000 cubic yards of contaminated concrete rubble will require disposal This work plan is designed to provide information to predict how concrete will behave at RFETS over a 1,000-year assessment period The Rocky Flats Cleanup Agreement (RFCA) defines limits for radionuclide contamination that must be met by any future on site disposal of concrete at RFETS Two main criteria are defined by the RFCA

- Contamination of groundwater and surface water
- Contamination of subsurface and surface soils

This report provides a qualitative discussion of the likely behavior of concrete compared to that of soils at RFETS, which is relevant to the application of soil action levels to disposed concrete The report also discusses how plutonium, americium and uranium concentrations in concrete can be defined which will be protective of water quality standards defined in the RFCA Finally, the report describes a program of experimental and modeling work where by these problems can be answered in a more quantitative manner

The basis of this work plan was a comprehensive review of the open literature on processes relevant to concrete degradation and plutonium, americium and uranium leaching from cementitious materials under the geochemical conditions at RFETS The majority of the open literature in this field is focused on the mobility of radionuclides in cementitious wasteforms and repository backfill materials Very limited information regarding actinide leaching from cement was found, as a consequence of its very low mobility and the need for long time scale experiments Much of the information regarding radionuclide leaching and diffusion is not directly relevant to concrete at RFETS because contamination here is largely surficial and not limited by diffusion through a cement matrix Because of the surficial nature of the contamination the review concluded that release of plutonium, americium and uranium from concrete might be considered to be controlled by the solubility of the contaminant on the surface and by processes of sorption on to the degraded concrete surface The predominance of one mechanism over the other is an important factor in determining the long term leaching behavior, and is dependent on the concentration of contamination on the concrete surface Much of the proposed experimental work described in this document is concerned with investigating this issue

The literature review showed that a reasonable prediction of the degradation of concrete at RFETS could be made, and that the main degradation mechanism would be by carbonation, the reaction with carbon dioxide in soil gases The chemical conditions resulting from surface carbonation of concrete will not be typical of the high pH low pe (Eh) conditions deliberately engineered in radioactive waste repository designs It is emphasized that because of these differences in chemistry, and the surficial nature of contamination, that plutonium, americium and uranium are likely to be more mobile in RFETS concrete than in most waste repositories

Comparison of the properties of RFETS soils and degraded concrete suggest that actinide contamination on concrete will behave similarly to that present in soils In particular, reported plutonium, americium and

uranium distribution coefficients between the aqueous and solid phases are generally similar for RFETS soils and concrete Contamination on concrete is however less likely to be transported by processes of wind erosion because carbonation is reported to produce a durable surface Actinides could be incorporated in alteration products of concrete, which would result in reducing their mobility, however such processes remain to be investigated

From the literature review, and considering the exposure routes used in determining the RFCA soil action levels, a comparison of the likely behavior of concrete and soil over 1000 years has been made From consideration of the structural integrity and likely degradation mechanisms influencing long term behavior, it is apparent that contamination on concrete will produce a lower risk than the equivalent concentration on soil In the worst case, where concrete is totally disaggregated, behavior would be identical to soil The major exception and area of uncertainty is knowledge of the chemical form of plutonium in concrete during the 1,000 year assessment period, and the work plan is designed to reduce this uncertainty

The definition of concentrations of plutonium, americium and uranium present in concrete that is protective of water quality standards has been evaluated by considering the solubility of possible contaminant material under RFETS groundwater conditions These calculations have shown that in order to comply with RFCA action levels these contaminants must be present at concentrations several orders of magnitude below their solubility limit Below the solubility limit the concentration of plutonium, americium and uranium in groundwater is controlled by their sorptive properties There is however insufficient knowledge of the sorption behavior and distribution coefficients of these actinides onto the surface of degraded concrete for a more quantitative assessment to be made at this stage

An experimental program has been designed to gather information to fill gaps in the literature, and to collect data directly relevant to the leaching of plutonium, americium and uranium contamination from the surface of concrete Two types of leaching experiments have been devised

1 Leaching of a range of concentrations of surface contamination from three types of weathered concrete under conditions of RFETS groundwater, to provide leach rate and solubility limits of plutonium, americium and uranium contamination

2 Enhanced leaching of a range of concentrations of surface contaminated concrete under varying pH conditions, to obtain a phenomenological understanding of leaching and sorption controls as a basis for predicting the behavior at RFETS over likely conditions during the 1,000 year risk assessment period

At this stage it is not known what samples, if any, of RFETS contaminated concrete may be available for experimental study, or their ranges in activity If samples are available, leaching experiments under RFETS conditions should be carried out In addition some preliminary surface characterization should be carried out using electron microscopy techniques, this should provide information relevant to the comparison to the behavior of soils, and the conceptual understanding of the solubility controls of the contaminants As RFETS samples may be limited, artificially contaminated unweathered and weathered concrete should by used in leaching studies In addition, it is proposed to perform accelerated weathering (carbonation) of an artificially contaminated concrete to examine the possibility of further immobilization of actinides by incorporation into the altered concrete The behavior of the actinides during such accelerated weathering is relevant to the application of RFCA action levels for both soils and for groundwater

The results of the proposed leaching experiments will be used to provide a quantitative assessment of the concentration of plutonium, americium and uranium in concrete that are protective of water quality Such calculations should include hydrological information together with preliminary details of the radionuclide inventory and the disposal design It is proposed that these calculations, coupling the effects of radionuclide leaching and transport are carried out using a computational model From this model, it will be possible to estimate the amount of concrete that could be disposed without exceeding water quality limits Clearly geochemical considerations are not the only constraint in controlling water quality and a quantitative assessment must also consider hydrological and design features over the assessment period

An estimate of the overall performance budget for this work plan and a schedule of the experimental and modeling tasks are provided

2. Introduction

This report provides a draft work plan describing a scope of work to test the short term and long term environmental effects of plutonium, americium and uranium contaminated concrete at the Rocky Flats Environmental Technology Site (RFETS) The background to this work is that, following decommissioning activities at RFETS, it is anticipated that 120,000 cubic yards of concrete rubble contaminated with plutonium, americium and uranium will require disposal (RMRS, 1998) Regulatory limits for clean up of RFETS have been defined in the Rocky Flats Cleanup Agreement (RFCA) (DOE, 1996a) Standards are defined in the RFCA based on contamination of soil and on water quality and must be demonstrated for a period of 1,000 years

The work plan described in this report uses current information available in the literature to qualitatively assess the physical and chemical properties of plutonium, americium and uranium when bound in concrete and to answer the questions "Does concrete behave like soils at RFETS over the 1,000 year assessment period? If not, how is concrete different from soils?" In addition the fate and transport properties of plutonium, americium and uranium will be qualitatively examined to answer the question " What concentration of plutonium, americium and uranium may be bound in concrete left at RFETS after decommissioning that will be protective of water quality standards?"

Following a literature review the work plan is developed to fill gaps in the literature and to test data in the literature so that a more quantitative answer can be given to the above questions

2.1 Basis of Work Plan

A literature review has been undertaken examining two main aspects relevant to the environmental behavior of plutonium, americium and uranium contaminated concrete

1 A review of likely chemical, physical and biological processes that will cause deterioration of concrete rubble, under groundwater and climatic conditions prevailing at RFETS

2 A review of plutonium, americium and uranium leach rate data from cement and concrete This included consideration of plutonium, americium and uranium solubility and sorption behavior under chemical conditions of concrete degradation at RFETS

The degradation of cement and concrete is important to the mechanical erosion and subsequent removal of surface radionuclide contamination and also to the chemical evolution of the surface layer The latter will influence both the solubility of plutonium, americium and uranium particulates in contact with groundwater and the sorptive properties of the dissolved radionuclides A summary of the literature review is provided in Section 3, and the review is included in Appendix A

Development of the work plan and a preliminary qualitative assessment of the limits of contaminant concentration in concrete require that a certain level of understanding and knowledge of the disposition of contaminated concrete at RFETS is available RFETS site data and issues which are currently *unavailable* to this review are

1 Ranges of radioactivity levels of contaminated concrete that may potentially be considered for disposal by burial at RFETS
2 Availability of samples of RFETS contaminated concrete for leaching and characterization experiments
3 Preliminary structural designs of any proposed concrete burial sites and remaining foundations
4 Hydrogeological behavior of such a site

This information would be required if the work plan described in this report were to be carried out to provide a quantitative assessment of the behavior of contaminated concrete at RFETS

2.2 Summary of Requirements of Rocky Flats Cleanup Agreement

The Rocky Flats Cleanup Agreement (RFCA) (DOE, 1996a) defines action levels and standards framework (ALF) for surface water, ground water and soil Action levels are defined at two levels

Tier I action levels are numeric values which when exceeded trigger evaluation, remedial action, and/or management action

Tier II action levels are numeric values which when met do not require remedial action and/or institutional controls

2.2.1 Soil Action Levels

For surface and subsurface soils, radionuclide action levels are defined by a 15mrem/yr dose for unrestricted land use and an 85mrem/yr dose for restricted land use These dose limits were converted to isotope activity levels (pCi/g) using the RESRAD computer code, considering two exposure scenarios, open space exposure in the buffer zone, and office worker exposure in the industrial area The RFCA recommends that the Tier I action level for surficial solid in the buffer zone is that of the 85mrem/yr level for residential exposure, and that for surficial soils in the industrial area the Tier I action level is that of office worker exposure at the 15 mrem/yr level The RFCA working group further recommend that the Tier II action level for the whole site is the 15mrem/yr level for residential exposure The current recommendation of the RFCA (DOE, 1996b) for subsurface soils is that the Tier I and Tier II action levels for surface soil are conservatively applied Table 1 provides a summary of the activity limits for soils defined by the RFCA (Source, Table ES-1 DOE, 1996b)

Radionuclide	*Tier I Action Level Buffer Zone (pCi/g)*	*Tier I Action Level Industrial Area (pCi/g)*	*Tier II Action Level Whole RFETS (pCi/g)*
Am 241	215	209	38
Pu 239/340	1429	1088	252
U 234	1738	1627	307
U 235	135	113	24
U 238	586	506	103

Table 1 Tier I and II soils action levels for RFETS

2.2.2 Surface Water and Ground Water Action Levels

Action levels for ground water and surface water are defined with reference to maximum concentration limits (MCLs) MCLs are risk based (10^{-6} increased risk to human health from exposure and consumption) The surface water quality standards and action levels are (DOE, 1996a, Appendix 5 Table 1)

- Pu 0 15pCi /L
- Am 0 15pCi /L
- U 10 0pCi/L

For groundwater, a Tier I action level is defined as 100 x MCLs which is designed to identify high concentration ground water sources that should be addressed through an accelerated action Tier II action levels consist of the MCLs, which are designed to prevent surface water from exceeding surface water standards by triggering ground water management actions The groundwater action levels are given in Table 2 sourced from Table 2 of appendix 5 DOE (1996a)

Radionuclide	*Tier I, 100 x MCLs (pCi/L)*	*Tier II MCLs (pCi/L)*
Am 241	14 5	0 145
Pu 239	15 1	0 151
Pu 240	15 1	0 151
U 233+daughters	298	2 98
U 234	107	1 07
U 235 +daughters	101	1 01
U 238 +daughters	76 8	0 768

Table 2 Tier I and II groundwater action levels for RFETS

2.2.3 Application of Action Levels to Proposed Disposal of Concrete at RFETS

The RFCA does not specifically consider the disposal of contaminated concrete at RFETS However it has been proposed (RMRS, 1998) that one possible standard for use with concrete is the Tier I soil action level defined in the RFCA The Building Closure Radiation Standards Workgroup (BCRSW) has determined that the 15/85 mrem/yr methodology may be met if the volume contamination in building concrete does not exceed the Tier I soil action level (Table 1) An objective of this draft work plan report is to evaluate the assumption used in the BCRSW determination that concrete behaves like soil, and to propose a work plan to provide further information if required

Another standard that must be considered is that radionuclides leached from disposed concrete must be protective of surface water quality standards, and the Tier II action levels for groundwater (Table 2) This study makes a preliminary qualitative assessment of how contaminant levels in concrete can be related to these water quality standards and action levels to define a limit for the concentration of plutonium, americium and uranium that may be bound in concrete at RFETS A work plan is designed so that these limits may be more quantitatively examined

3. Literature Review of behavior of contaminated concrete

Appendix A of this report contains a comprehensive literature review of the behavior of plutonium, americium and uranium in cementitious environments, with particular reference to the surface contamination to be found at the RFETS The purpose of this review was twofold

1 To formulate a qualitative interpretation of the behavior of buried contaminated cement

2 To identify gaps in data/knowledge, which in turn will drive the design of a work plan, to more fully understand contaminant behavior at RFETS

The literature survey covered all aspects of cement and concrete behavior under environmental conditions, including physical and chemical degradation processes, microbially induced degradation, leaching behavior of actinides and general behavior of actinides in cementitious environment (such as solubility and sorption) The vast majority of the literature on this subject is concerned with *encapsulation* of radioactive waste products for disposal in a repository scenario However, it is possible to utilize the understanding of the physico-chemical basis of contaminant-concrete interactions from these encapsulation studies to build a qualitative picture of the likely behavior of the *surface* contaminants at RFETS

3.1 Summary of Review

The proposed use of cementitious waste forms as part of the multi-barrier approach to radioactive waste disposal means that there is a large body of work concerned with the long term behavior of cements and concrete under environmental conditions From this information, in conjunction with the RFETS Sitewide Geoscience Characterization study, it has been possible to qualitatively predict the degradation of buried concrete rubble at RFETS, and to pinpoint the chemical controls on the leaching behavior of plutonium, americium and uranium

The hydration of cement mixtures leads to the formation of a number of chemical phases, of which the most important are calcium hydroxide and calcium silicate hydrate (CSH) Leaching of these two phases results in high alkalinity/high pH porewater solutions, the extent of which depends on the initial composition of the cement, extent of degradation and the composition of the ingressing water These reactions form the basis of the use of cementitious wasteforms in repository design

The permeability of concrete is low compared to soil material, and so flow through concrete blocks buried with soil will be small, with the predominant flow being concentrated around the outside of the blocks Actinide contamination of buildings concrete is predominantly on the surface, or within the first few millimeters of the surface Release of contamination will not therefore be retarded by the slow diffusion of actinides through the cement matrix, which is a feature of the use of cement based materials in encapsulation of radioactive waste As the contamination at RFETS is present in the first few millimeters of concrete, the mobility of the radionuclide contamination, and subsequent leaching behavior, will be controlled by the degradation of the concrete surface A number of mechanisms can impact on the degradation of cements, with the extent of each degradation mechanism being dependent on the local geochemical conditions Thus, these mechanisms have been examined with reference to RFETS contamination

The background groundwaters at RFETS, certainly in the upper hydrostratigraphic unit are characterized as calcium bicarbonate waters As the thickness of this unit is between 10 and 130 ft , it is likely that any buried concrete rubble will be in contact with this water Thus, the main process of degradation is likely to be carbonation, the reaction of carbon dioxide either in soil gases or dissolved in groundwater Carbonation of the surface of the buried concrete may result in a more durable surface, more resistant to freeze-thaw and mechanical erosion In addition, permeability is also decreased The groundwater composition does not point to chloride, magnesium or sulfate attack being important, apart from in the industrial area, where sulfate levels are in excess of 1000mg/l However, the main impact of sulfate attack, and also corrosion of steel rebar, is to induce cracks in concrete structures, this can be important for encapsulated waste, where cracks can expose the waste to percolating groundwater As the contamination at RFETS is surficial in nature, sulfate attack, even if it occurs, is unlikely to impact on the leaching behavior of radionuclides at RFETS Microbially induced degradation of concrete, through the oxidation of sulfide into sulfuric acid by *Thiobacilli* species, has also been examined However, the presence of sulfides in the local alluvium and bedrock, and the lack of evidence for any sulfide oxidation, appears to confirm that microbial influence on concrete degradation will be limited, unless some other form of reduced substrate, such as organic carbon is disposed with the buried concrete

In terms of radionuclide behavior at the surface of the concrete, the main effect of carbonation is to lower the local fluid pH, from around 12 (for a fresh cement) to approximately 8 Redox conditions will be unaffected by carbonation, and so local redox conditions are most likely determined by that of the background geochemistry Thus, it must be emphasized that the likely conditions to be found on the surface of buried concrete at RFETS will be significantly different from the extreme high pH, low pH conditions deliberately engineered in radioactive waste repository designs This means that plutonium, uranium and americium will likely be more mobile in RFETS concrete than in such repositories

Experimental studies of the leaching behavior of plutonium, uranium and americium from cementitious materials are very limited, due to the low mobility of actinides under these cementitious repository conditions, and the consequent need for long term experiments The vast majority of these studies are concerned with leaching from cement encapsulated waste, where diffusion controls can be important However, for RFETS contaminated concrete, the contamination is close to the surface, and so diffusive control is unlikely to be important Instead, leaching from the surface is considered to be controlled by processes of sorption onto the degraded cement surface, and where concentrations are sufficiently high, by solubility control from a solid contaminant, such as PuO_2 Given this, a review of actinide solubility and sorption under cementitious conditions has been undertaken A large body of literature exists concerning these behaviors, although the majority is concerned with higher pH's than relevant here However, a good understanding of the controls on solubility and sorption is possible Actinide distribution coefficients (R_d or K_d, representing the ratio of sorbed to aqueous concentrations, see List of Acronyms, Abbreviations and Symbols) are generally high for sorption onto cements, although these mainly relate to high pH, non-carbonated cement substrates Actinide sorption is generally less strong at lower pH, but the uptake of contaminants onto carbonated cements is more uncertain In particular, the formation of co-precipitates with calcium carbonate would result in contaminants being less accessible to the groundwater However, the probability of this occurring is unclear at the moment Experimental studies indicate that the solubility of actinides is crucially dependent on the pH, the presence of carbonate and the nature of the solid phase

In summary, as a result of the literature survey, a reasonable understanding of the degradation of concrete at RFETS is possible However, the mobility of plutonium, uranium and americium under the chemical conditions established in the degraded concrete is more uncertain It is clear that it is not possible to extract leaching data directly from cementitious waste form experiments, due to the difference in relevant geochemistry and nature of the contamination

The following conclusions can be made

1 Carbonation of the concrete surface will be the dominant degradation mechanism,
2 The surface of the concrete at RFETS will exhibit lower pH's than would be expected in an engineered repository,
3 There are no leach data from the literature that can be directly applied to RFETS contamination,
4 Mobility of actinides at RFETS will be higher than would be experienced in an encapsulated cement wasteform,
5 Mobility of actinides at RFETS will be determined by sorption and solubility considerations, depending on concentration,
6 There is uncertainty of both solubility and sorption mechanisms likely to be predominant for surface contaminated concrete

3.2 Gaps in the Literature

As has been alluded to above, the literature review has not been able to find any leach data that can be directly related to RFETS contaminated concrete There is a general lack of actinide data for leaching from concrete, and the few available studies are centered on encapsulated waste It is clear that this does not describe RFETS contamination very well

The open literature does not contain information concerning the form of uranium, plutonium and americium on the surface, and near to the surface, of contaminated construction concrete This is an important consideration for understanding the leaching behavior at RFETS, as the form of the contamination will, to a large extent, determine the mechanism responsible for actinide release from the concrete surface

Most, if not all, the literature studies on actinide mobility in cementitious environments have focused on diffusion through a cement matrix Allied to these studies, work detailing solubilities and sorption have been used to determine the rate of release from encapsulated cement wasteforms Thus, explicit experimental studies of the leaching behavior of actinides from the *surface* of concrete, particularly carbonated cements, are non-existent

It is possible that some of the open literature data and information can be used to paint a qualitative picture of leaching behavior If desired, a more quantitative idea can be obtained, using, for example, derived solubility limits or R_d's from the literature An example of this is described later, where the results of geochemical modeling have been used to derive leached concentrations as the result of dissolution of actinide mineral phases under cementitious conditions However, this approach is fraught with difficulty, and currently the uncertainties are enormous For example, the form of the mineral phase is crucial, if solubility is the determining factor for leaching behavior Therefore, although the behavior of actinides under various conditions can be understood from information derived from the literature, a major uncertainty exists in relating this to RFETS

In summary, the following lists the questions that need to be answered if the leaching behavior of contaminated concrete is to be understood

a) What is the form of contamination on surface, e g

  i) adsorbed

  ii) discrete contaminant particles, such as PuO_2 or

  iii) incorporated in the cement mineral phases?

b) What is the mechanism determining actinide leaching?

  i) solubility or

  ii) desorption

c) How does leaching behavior change as a result of variations in RFETS site conditions, in particular,

  i) what is the effect of carbonation?

  ii) what is the effect of contamination concentration on the surface?

  iii) what is the effect of variations in site geochemistry, such as pH?

None of the above can be answered with reference to the open literature, and so this Task Plan is focused on these questions If answered, it will be possible to determine the concentration of plutonium, americium and plutonium that can be disposed at RFETS bound to concrete while being protective of water quality standards

4. Qualitative assessment of behavior of concrete contamination

4.1 Comparison to behavior in soil

It has been discussed previously (see section 2 2 3) how Tier I soil action levels could be used to define volume concentration limits of actinide contamination in concrete In order to assess the applicability of the Tier I soil action levels to radionuclides present in concrete at RFETS the following questions have been posed

"Does concrete behave like soils at RFETS over the 1000 year assessment period?"

"If not, how is concrete different from soils?"

In order to answer these questions it is necessary to briefly review the properties of RFETS soils with regard to their sorptive properties for the actinides and for possible transport processes operating in soils These can then be compared to comparable properties of concrete

4.1.1 General properties of RFETS soils

The surface sediments at RFETS are Pleistocene to Holocene alluvial deposits The alluvial deposits are poorly sorted and contain various lithologies ranging from silty clay to silty sand with pebbles and cobbles (EG&G, 1995a) The majority of this alluvium is likely to be sourced from the underlying Cretaceous claystone, siltsone and sandstones, which have been described in detail in the Geological Characterization Report (EG&G, 1995b) The Cretaceous formations are composed mainly of quartz with lesser amounts of potassium feldspar, plagioclase, mica/illite and kaolinite The clay-size fraction, which constitutes 2 to 7 percent of the total, is mainly composed of illite/smectite and kaolinite with minor illite, chlorite and gibbsite The illite/smectite is smectite-rich containing 10 to 15 % illite Weathered samples of bedrock contain secondary iron-oxides/hydroxides The presence of smectitic clay minerals and iron-oxides/hydroxides in the bedrock source would suggest that the RFETS soils would have generally good sorptive properties

A characterization study of Pu contaminated soils at RFETS (Honeyman and Santschi, 1997) calculated distribution coefficients (K_d's) in the range $1x10^4$ L/kg to 1 $2x10^5$ L/kg Somewhat lower Kd's are recorded elsewhere for data used in a risk assessment exercise (RMRS, 1996) RFETS Site data Kd's for Pu are 100 L/kg for the vadose zone and 20 L/kg for the saturated zone, and are at the low end of the range reported in the same study for soil "literature values" Americium has comparable K_d's to Pu in this database (RMRS, 1996), while uranium has values of 17 and 2 L/kg for the vadose and saturated zones respectively Honeyman and Santschi (1997) determined Kd values for uranium to be in the range 30 to 180 L/kg for solar pond core isolates under oxidizing conditions

Reports of the nature of Pu in contaminated soils indicates that it is present in the form of very fine grained particulate oxide ranging in size from a mean size of 0 08μm in the eastern buffer zone to a mean of 0 3μm in the 903 Pad contamination source area (DOE, 1996b) A study of the distribution of Pu in Rocky Flats soils (Little and Whicker, 1972) concludes that the main mechanism of environmental dispersion is by wind transport of plutonium oxide agglomerated with soil particles Honeyman and Santschi (1997) similarly concluded on the basis of the very high Pu distribution coefficients measured that transport of plutonium under oxidizing conditions would be primarily through mechanical erosion, but that U(VI) may be subject to groundwater transport

4.1.2 Comparison to likely behavior of concrete

A review of the likely degradation behavior of disposed buildings concrete at RFETS is provided in Appendix A and is summarized in section 3, the following discussion draws from this review The degraded concrete is likely to be composed of calcite together with poorly crystalline silica resulting from the carbonation of the surface of concrete blocks The degraded concrete surface, where the plutonium, americium and uranium contamination mainly resides will therefore have a quite different mineralogy to the RFETS soils described above, and may therefore exhibit different sorptive properties A review of the distribution coefficients of plutonium, americium and uranium onto cementitious materials is provided in Appendix A, Table 2, R_d's listed here are typically in the range 1,000 to 20,000 L/kg and thus comparable to some of the high distribution ratios reported for RFETS soils The values listed in Appendix A, Table 2 are, however, for undegraded cement matrices composed of CSH minerals, which can have a large surface area For degraded concrete distribution coefficients for calcite may be more appropriate, and these are lower, U 20L/kg, Pu, Am 400-5,000 L/kg (Appendix A) Overall it appears that the surfaces of degraded concrete rubble would have similar distribution ratios to RFETS soils

Actinide contamination of buildings concrete is predominantly on the surface, or within the first few millimeters of the surface Release of contamination will not therefore be retarded by the slow diffusion of actinides through the cement matrix, which is a feature of the use of cement based materials in encapsulation of radioactive waste In this regard surface contaminated concrete rubble must be considered comparable to contaminated soil, where particulate material is present on soil particle surfaces Carbonation of the surface layers of concrete rubble is likely to produce a more durable material with reduced porosity which is more resistant to mechanical erosion and degradation by processes such as freeze-thaw Where carbonation occurs, subsequent to the contamination particulates could be more firmly entrapped in a calcite matrix, although this remains to be demonstrated Contamination on the surface of concrete is therefore less likely to be subject to mechanical erosion and dispersion by wind and fluvial transport processes than equivalent contamination of RFETS soils

The nature of plutonium, americium and uranium contamination on the surface of RFETS concrete is unknown Contamination resulting from plutonium combustion may initially have been in the form of plutonium oxide particulates, however such material could conceivably react with the cement matrix minerals of the concrete and be present as a trace component in calcite formed as an alteration product Research in this area is somewhat ambiguous (Appendix A) Other possible actinide alteration products include silicate phases such as uranophane (Appendix A) Contamination from nitrate solution may also produce more complex phases by reaction with cement minerals and calcite Because cement minerals in disposed concrete will be actively reacting with groundwater then it is more likely that actinides are chemically incorporated into the stable cement alteration products Soil minerals however will be less reactive and therefore less likely to incorporate actinide contamination

Transport of radionuclides in groundwater can be enhanced by sorption onto colloidal material, and subsequent migration of the colloidal particles in groundwater (Appendix A) The colloid enhanced radionuclide transport can be significant if it can be shown that

- Colloids are present in significant quantities,
- The colloids are able to sorb radionuclides,
- The colloids are stable in solution, and
- Sorption is irreversible

This level of detail is not currently available for possible colloid generation at RFETS However, if a worse case scenario is assumed, whereby colloids are present in sufficient quantities and are stable in the local groundwater, the ability of colloids to significantly increase radionuclide mobility depends on the ability of the colloid to out-compete the much larger surface area of static substrate surfaces for sorption of the radionuclide (Bradbury and Sarott, 1994, Appendix A) The most likely colloidal materials generated from degraded concrete are mobile silica phases resulting from leaching of the cement matrix, and corrosion products of steel rebars For these colloids to be effective then they must be able to sorb significantly more radionuclides than the RFETS soils, and any natural colloids that could be present in RFETS groundwater Since RFETS soils appear to have similar distribution coefficients to degraded concrete then colloids generated from disposed concrete are unlikely to significantly enhance radionuclide mobility in ground water Compared to other uncertainties, such as radionuclide leach rate from RFETS concrete, detailed examination of concrete derived colloids is not justified at this stage

In summary, from available literature information, the following preliminary conclusions can be made regarding the comparative behavior of contaminated concrete and soils at RFETS

- Although different retardation processes are likely to be operating, the distribution coefficients for actinide sorption onto degraded concrete and soils are comparable
- Degraded concrete is likely to be more durable and less prone to mechanical erosion than soils This would be expected to reduce the dispersion of actinide contamination by wind and fluvial transport processes
- The exact nature of the actinide contamination on concrete is unknown, but it is possible that actinides are incorporated into stable cement alteration products Such a process would reduce actinide mobility at RFETS, however further research is required to confirm the nature of contamination on concrete
- Generation of colloidal material from degraded concrete could possibly enhance radionuclide transport, but detailed study is not justified at this stage

4.1.3 Application of Soil Action Levels to disposed concrete

The definition of Soil Action levels in the RFCA and the proposal to apply these limits to the disposal of plutonium, americium and uranium contaminated concrete at RFETS has been summarized in section 2 2 To make a comparison of the behavior of concrete and soil at RFETS relevant to the application of soil action levels to concrete it is necessary to compare how the risk assessment exposure routes may be affected The exposure routes considered by the risk calculations for soil were (DOE, 1996b)

1 Ingestion
2 Inhalation
3 External exposure

Radiation dose to an individual was calculated using appropriate Dose Conversion Factors (DCF) The DCF for each exposure route differs with the chemical form of the radionuclide The chemical form for americium, uranium and all daughter products were chosen conservatively so that the DCF would be maximized for each exposure route (DOE, 1996b) The DCFs for plutonium were chosen based on the oxide form (DOE, 1996b) Thus, to answer the question " Does concrete behave like soil at RFETS over the 1,000 year assessment period? If not, how is concrete different from soils?" consideration must be given to the three exposure routes, and the chemical form of the plutonium contamination

Firstly considering the external exposure route, the contamination of both RFETS concrete and of soil is considered to be on the surface, thus there is unlikely to be any effective difference in the absorption of gamma radiation by concrete or soil The dose received from the external exposure route should therefore be the same for concrete and soil

The ingestion and inhalation exposure routes are both dependant on the physical and degradation behavior of concrete The literature review has provided an important understanding of the likely degradation behavior of concrete left at RFETS over a 1,000 year period and following points are evident

1 The main chemical degradation process affecting the concrete is carbonation, the literature review has shown that carbonated concrete and analogues remain durable for periods exceeding 1,000 years The durability of carbonated concrete will reduce the likelihood of the production of fine-grained material containing plutonium, americium and uranium, which will reduce the dose through the ingestion and inhalation pathways
2 Review of long-term modeling of the integrity of large concrete structures used in repository designs, indicate that structures are likely to remain intact for periods around 1,000 years Disposed concrete rubble is therefore likely to remain during the 1,000-year risk assessment period at RFETS and is unlikely to be disaggregated Again this will tend to reduce the dose through the ingestion and inhalation pathways
3 Freeze-thaw processes could lead to the spallation of the surface layer of concrete rubble, which is the site of the plutonium, americium and uranium contamination Such a process will tend to enhance the physical degradation of fine-grained material which will then be available to the ingestion and inhalation exposure routes The extent of freeze-thaw processes will depend on the exact disposition of the disposed concrete, and for instance will be reduced by burial, or capping Evaluation of the significance of freeze-thaw processes must take into account disposal designs

It can be concluded that because of its physical integrity concrete will contribute a lower amount of radionuclides to the inhalation and ingestion exposure routes than an equivalent loading of soil In the case of uranium and americium since conservative DCFs were chosen in the definition of soil action levels then concrete will produce a lower risk than soil In the worst case, of complete disaggregation of concrete to soil grain size, the risk from uranium and americium contamination on concrete will be the same as that on soil

For plutonium the DCF was based on the assumption that plutonium was present as the oxide Current information available in the literature is insufficient to conclude whether this assumption is valid for plutonium contaminated concrete at RFETS It is possible that plutonium contamination present in concrete may behave differently than that present in soil and may be in a different chemical form than the oxide It has been discussed elsewhere in this work plan what other forms the plutonium may exist in the local chemical environment of the concrete If the chemical form of the plutonium had a higher DCF than plutonium oxide used in determining the soil action levels then the action level for plutonium would have to be lowered to comply with the same risk criteria To address this area of uncertainty the work plan has been developed to attempt to identify the chemical form of the plutonium present on contaminated RFETS concrete, and to investigate the fate of this material during carbonation of the concrete

One problem in comparing action levels of soil with those appropriate for buried concrete is that the action levels defined in the RFCA are defined in terms of activity per gram, which can be related to an activity per volume of soil However, as the contamination of RFETS concrete is surficial in nature, appropriate action levels should be expressed in terms of activity per unit area This means that the inventory of disposed concrete needs to take into account the likely geometry and size distribution

In summary, from the literature review, and considering the exposure routes used in determining the RFCA soil action levels it is apparent that concrete will likely behave better than soil in regard to soil action levels In the worst case, where concrete is totally disaggregated, behavior would be identical to soil The major exception and area of uncertainty is knowledge of the chemical form of plutonium in concrete during the 1,000 year assessment period, and the work plan is designed to reduce this uncertainty

4.2 Behavior relative to water quality standards

In the light of the findings of the literature review, it is possible to discuss, at least qualitatively, the leaching behavior of RFETS contaminated concrete, and answer the question "What concentration of Pu, Am and U may be bound in concrete left at RFETS after decommissioning that will be protective of water quality"

The leaching mechanism governing release of actinides from a concrete surface can be crucially dependent on the concentration of contaminants on the surface Figure 1 provides an illustration of the relationships between radionuclide concentration on the concrete surface, and the concentration in groundwater, when either solubility controlled or sorption controlled

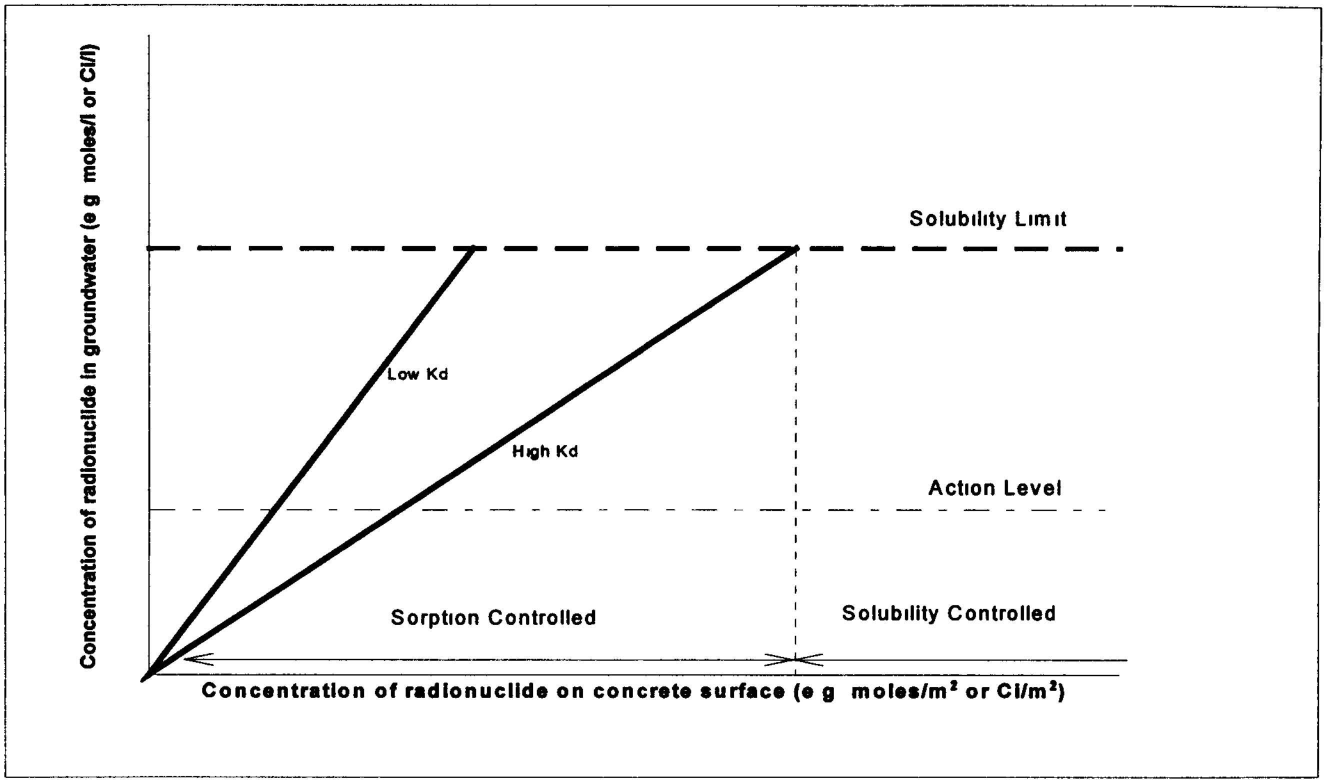

Figure 1 Diagrammatic representation of controls of radionuclide concentration in groundwater by solubility and sorption control, and likely relation to Action Level

When the groundwater radionuclide concentration is sorption controlled the groundwater concentration can be determined by a distribution coefficient (K_d, or R_d) which is the ratio of the concentration of radionuclide sorbed to the equilibrium concentration in the solution In Figure 1, the K_d is the reciprocal of the slope of the diagonal lines Thus the concentration of radionuclide in concrete that is protective of water quality standards can be estimated For soils, K_d is usually expressed in units of mass of soil per volume of water, however for release from the surface of contaminated concrete rubble it is perhaps more appropriate to express the distribution coefficient in terms of the macroscopic surface area of concrete, and this can be directly determined from surface leaching experiments

The literature review considered sorption coefficients for uranium, plutonium and americium onto cement phases, and concluded that lower sorption is exhibited by radionuclides onto carbonated concrete, than onto fresh concrete The R_d's available in the literature are of similar magnitude to those used in Rocky Flats assessments, and so the distribution of actinides could be expected to be similar Major uncertainties exist, however, in assessing the partitioning of radionuclides in concrete systems, particularly the form of the contamination (nature of the particulates) and the question of whether the contaminants will be incorporated into the cement matrix In addition, any discussion of K_d's has to acknowledge the uncertainty associated with colloid partitioning Plutonium readily forms aggregates of polymeric aqueous species (true colloids), as well as associating with inorganic and organic particulates (pseudocolloids) Therefore it is especially important to address the question of colloid partitioning when determining sorption distribution coefficients, particularly with reference to phase separation techniques A further discussion of the role of colloidal transport at RFETS can be found in Sections 5 8 and 7 2 of the literature review (Appendix A)

As shown in Figure 1, if the concentration of contaminants is sufficiently high, the leaching behavior will be controlled by the dissolution of a solubility controlling solid phase Therefore, using solubility data from the literature and geochemical modeling codes it is possible to predict the concentrations of Pu, Am and U resulting from the dissolution of surface particulate contamination These concentrations, which can be considered an upper limit, can then be compared to the RFCA Tier I action level for ground water contamination, and the Tier II action level for protection of surface water quality

Full details of the geochemical modeling results are given in Appendix B, and the main features are summarized here Solubility limits were calculated for uranium, plutonium and americium, under two distinct conditions

1 In equilibrium with fresh cement (approximated by $Ca(OH)_2$),
2 In equilibrium with carbonated cement (approximated by calcite)

The literature review revealed that the solubility of radionuclides in cementitious environments is crucially dependent on the solubility limiting solid phase Consequently, solubility calculations were undertaken considering a number of likely phases

Table 3 shows the results of the solubility calculations, as well as the activities associated with these concentrations Isotopic compositions were taken from the Rocky Flats Cleanup Agreement (DOE, 1996b), with the exception of uranium, for which no information has been made available Therefore, the uranium activities have been calculated for each of the three isotopes, U-234, U-235 and U-238

The results show that the choice of solid phase is crucial If the results shown in Table 3 are compared to the groundwater action levels (see Table 2), it can be seen that only for PuO_2 (c) and $CaUO_4$ are the activities below the action levels However, the PuO_2 (c) thermodynamic data used in these calculations corresponds to a very crystalline solid phase, with consequent low solubility The more amorphous form, $Pu(OH)_4$, is seven orders of magnitude more soluble - this is the phase that would be expected to precipitate out of aqueous solution Therefore, it is important to establish whether the contamination at RFETS is in the form of crystalline PuO_2 particles, or a more amorphous phase A similar picture emerges for uranium, where the solubility of $CaUO_4$ is below the action levels, while the solubility of CaU_2O_7 is higher The mineral phase CaU_2O_7 has been identified as a solubility-limiting phase in cement leachates (Heath *et al*, 1997), whereas it is not clear whether CaUO4 forms under the same conditions Certainly, the thermodynamic data used in these calculations indicate that $CaUO_4$ is a crystalline solid phase Solubility experiments performed by Serne et al (1996) indicate behavior that would be expected by $CaUO_4$ solubility control However, the experimental concentrations were three orders of magnitude higher than those predicted by $CaUO_4$ solubility They concluded that "a more soluble phase of $CaUO_4$ (such as $CaUO_4$ (am), if it exists) is most likely the solubility-controlling solid" Therefore, there is much uncertainty in this area and it is impossible to conclude that uranium concentrations will be below the action levels

Pu	$Pu(OH)_4$	12 5	$7 4 \times 10^{-11}$	93 8% Pu-239, 5 8% Pu-240, 0 36% Pu-241	7663
Pu	PuO_2 (c)	12 5	$1 2 \times 10^{-18}$	93 8% Pu-239, 5 8% Pu-240, 0 36% Pu-241	0 07
Am	$Am(OH)_3$	12 5	$5 7 \times 10^{-11}$	100% Am-241	47080
U	CaU_2O_7	12 5	$1 2 \times 10^{-6}$	100% U-238 100% U-235 100% U-234	96 610 1746149
U	$CaUO_4$	12 5	$4 2 \times 10^{-14}$	100% U-238 100% U-235 100% U-234	$3 36 \times 10^{-6}$ $2 13 \times 10^{-5}$ 0 06
U	UO_3 H_2O	12 4	$1 5 \times 10^{-2}$	100% U-238 100% U-235 100% U-234	1200367 7620722 $2 2 \times 10^{10}$

Table 3 Calculated Solubilities of Pu, Am and U, in equilibrium with $Ca(OH)_2$

The results presented in Table 3 reveal that, even at the high pH's expected in a fresh cement leachate, the solubility limits result in activity levels that are too high, with respect to groundwater action levels, provided crystalline phases are not present The results of solubility calculations in a calcite environment are also shown in Appendix B, and reveal that solubility is higher than indicated in Table 3, even if the crystalline PuO_2 phase controls plutonium leaching behavior

The indicative calculations described above show that the groundwater action levels will be exceeded if contamination is present above the solubility limits of each radionuclide (assuming that crystalline solids are not formed) The calculated solubility limits in Table 3 show huge variation, as result of a lack of understanding of the nature of the solubility controlling phase Unless the solubility of representative plutonium, americium and uranium contamination on RFETS concrete is determined by leaching experiments, then the higher solubility limits in Table 3 must be used in any assessment exercise Below the solubility limit concentrations of radionuclides in groundwater will be controlled by sorption onto the surface of the concrete The concentration of radionuclides in groundwater resulting from concrete leaching is not solely a matter of consideration of distribution coefficients and solubility limits Hydrological information is also critical because the concentration in groundwater clearly depends on the volume into which a certain amount of radionuclide is dissolved Another consideration is the rate at which radionuclides are released from the concrete surface, particularly in fast flowing ground water Since generic data is not applicable to RFETS contaminated concrete, measurement of the rate at which radionuclides are leached from the surface of concrete is essential A quantitative assessment of the behavior of contaminated concrete at RFETS in relation to water quality standards therefore requires consideration of both geochemical and hydrological parameters An outline of the modeling methodologies required to perform such an assessment is described later in this Work Plan

In summary following the review of the literature on radionuclide leaching and solubility and sorption in cementitious systems the following conclusions can be made

1 To comply with RFCA action levels for groundwater and surface water plutonium, americium and uranium present in concrete must be at present at levels several orders of magnitude below their solubility limit when dissolved in groundwater
2 Current uncertainties in the distribution coefficients of plutonium, americium and uranium on carbonated concrete prevent calculation of the concentration of radionuclides in concrete that are protective of water quality standards
3 Quantitative assessment must combine data regarding radionuclide leach rate, solubility and sorption with hydrological information

5. Identification and description of phase II work

5.1 Overview of experimental work

The following section identifies and describes experimental work that is required to more quantifiably assess the behavior of contaminated concrete at RFETS A fully quantitative understanding of the behavior of contaminated concrete is dependant on the availability of samples of actual plutonium, americium and uranium contaminated RFETS buildings concrete for leach testing and other characterization work No information has been available to this review concerning the availability of such material, or the range of radioactivity in buildings concrete that may be considered suitable for disposal by burial at RFETS Given these constraints, and anticipating that the availability of contaminated RFETS building concrete may be restricted, the work plan has been designed to either include or exclude RFETS concrete samples Clearly, study of contaminated RFETS concrete samples is the preferred option in presenting a more justifiable case for the definition of realistic plutonium, americium and uranium concentrations in concrete that are protective of water quality It is however recognized that study of such material may not be possible at this stage As an alternative it is proposed to investigate the leaching characteristics of artificially contaminated concrete, at this stage it is anticipated that these experiments will yield a conservative estimate of the limits of contaminant concentrations in concrete

A summary of the experimental tasks is shown in Figure 2 Tasks 2 , 5, 6 and 7 are subject to contaminated RFETS concrete being available If only a small number of samples is available then priority should be given to task 6, which is designed to give the most critical information in regard to comparison with RFCA action levels Experiments on artificially contaminated concrete (tasks 3, 4, 6 and 7) should be undertaken regardless of the availability of contaminated RFETS concrete

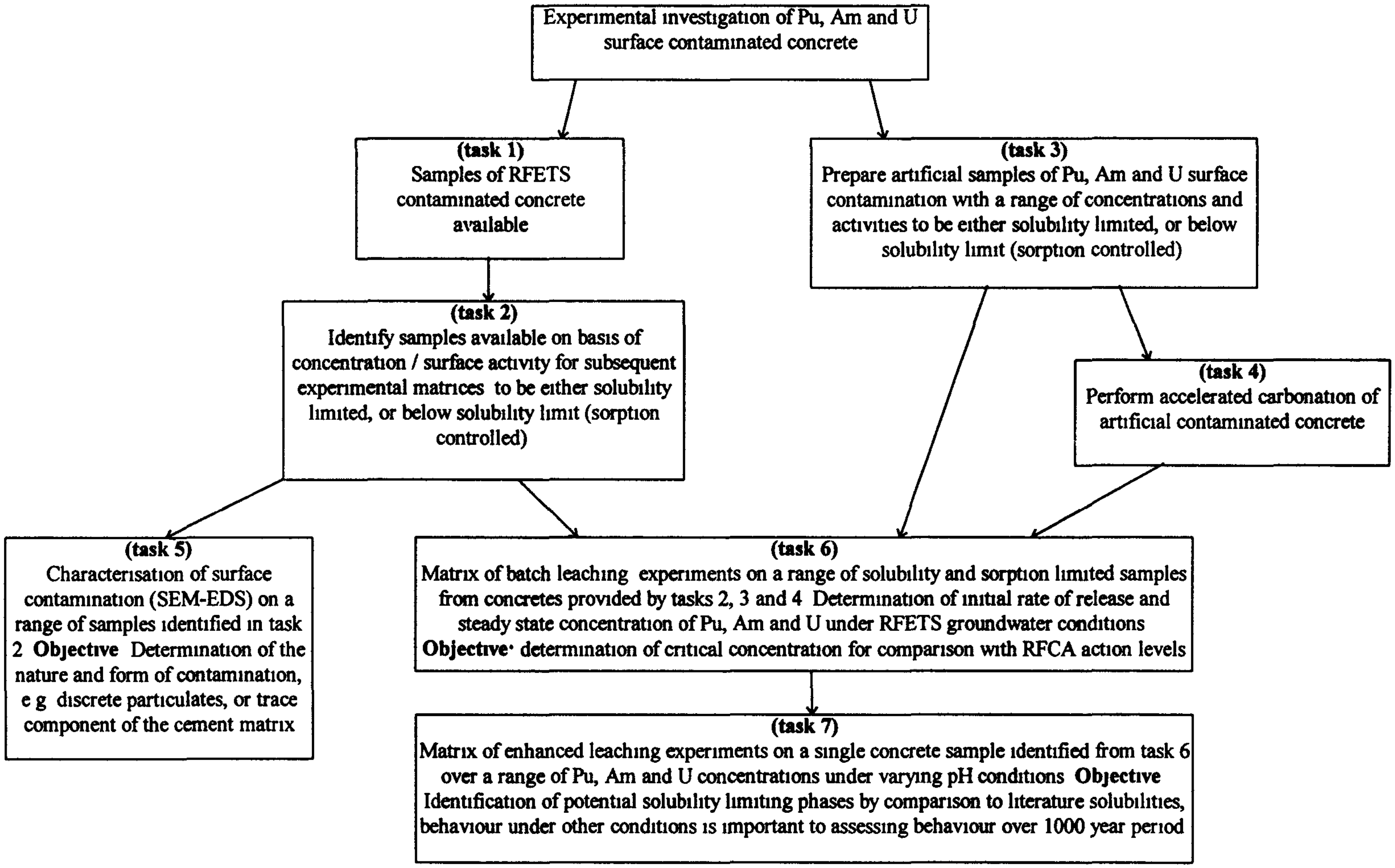

Figure 2 Summary of experimental studies in the proposed work plan

5.2 Sample preparation and selection criteria

5.2.1 Task 1 and Task 2: Contaminated RFETS concrete

Samples of contaminated RFETS concrete will be required to be selected for leaching experiments and surface characterization For the leaching experiments (tasks 6 and 7) a range of surface concentrations are required such that when samples are leached in a given volume of groundwater simulant, the amounts remaining in solution range from concentrations at a predicted solubility limit, down to concentrations below the RFCA action levels for groundwater, controlled by desorption The calculation of the concentration and activity of radionuclide on the surface that is at the solubility limit is outlined in Appendix B At concentrations below the solubility limit, the concentration of radionuclide is calculated with an estimate of the sorption distribution coefficient Concrete samples thus require selection based on an activity measurement per unit surface area (e g Ci/m^2) Therefore, an important part of Task 2 is the development of a sampling and analysis plan If information on RFETS building contamination is not available, it is obvious that a sufficiently detailed building survey is required, followed by a sampling program, for this part of the work plan to be implemented The feasibility and cost/time estimate of such a study is beyond the scope of this review

Samples for surface characterization (task 5) require relatively high levels of contamination and should be those identified as being solubility limited in the selection of samples for leaching Ideally samples for task 5 should be the same as those used in the leaching study

5.2.2 Task 3: Preparation of artificial contaminated concrete

Samples of artificially contaminated concrete should be prepared using samples of concrete which are representative of the cement matrix and aggregate of contaminated concrete at RFETS Ideally, such material should be available from uncontaminated concrete at RFETS Two types of concrete surface should be utilized

1 Weathered concrete, in which the surface has been previously carbonated prior to contamination Such a material is envisaged to be the surface of concrete exposed to the atmosphere for several years

2 Unweathered concrete with no carbonation, where the cement matrix is composed of CSH material This material could be the fresh surface of the same concrete as (1), but with the carbonated surface mechanically removed Fresh cured concrete should be avoided as this is unlikely to be representative of the state of RFETS concrete during contamination, and will contain excessive alkalis

Preparation of artificial plutonium, americium and uranium contamination on concrete resulting from Pu fires is unlikely to be practicable An alternative method is required as a necessary compromise if such RFETS contaminated concrete is not available for leaching studies Preparation of contamination resulting from liquid nitrate spillage and immersion is more feasible and the following approach is recommended

A solution containing dissolved plutonium, americium and uranium as a mildly acidic nitrate solution should be pipetted onto the surface of the concrete specimen The solution should react with the concrete surface where the acidity will be titrated by either calcite or CSH phases As a result of the pH change the radionuclides will precipitate on the surface Any residual radionuclide remaining in solution should be precipitated by drying the sample at 100 °C for several hours The volume of the pipetted solution should be kept at a minimum to avoid excessive uptake of liquid by the dry concrete, but should be sufficient so that the solution can be evenly distributed onto the concrete specimen The pH of the solution should be sufficient to solubilize the actinides, but should not contain excessive acid that carbonated surfaces are totally removed, or that subsequent carbonation is inhibited

The amounts of plutonium, americium and uranium pipetted onto a given area of concrete should be varied so that in the leaching experiments the target concentration achieved ranges from that of the likely solubility limit to below the RFCA action levels for groundwater This is the same criteria as used if samples of RFETS concrete are available for study (Section 5 2 1)

5.2.3 Task 4: Accelerated carbonation of contaminated concrete

Accelerated carbonation of artificially contaminated concrete should be undertaken to examine how the mobility of plutonium, americium and uranium may vary as a result of carbonation, the most likely long-term degradation process effecting buried concrete at RFETS It is possible that carbonation reactions may incorporate the actinide contamination in the resulting calcium carbonate matrix, which may then influence its release from concrete Studies have previously been performed investigating the effect of carbonation on cement microstructure (Houst, 1997) and the release of nitrate and strontium (Walton *et al*, 1997) Both these studies demonstrate that enhanced carbonation of cementitious materials is achievable under atmospheres at high humidity and CO_2 levels Walton *et al* (1997) found that 3 1cm diameter waste forms were fully carbonated after 26 days exposure to 50% CO_2 atmosphere at 75-50% relative humidity at a temperature of 50°C Houst (1997) states that the most favorable conditions for carbonation are 80-90% CO_2 and 76% relative humidity Accelerated carbonation should be carried out on samples of unweathered concrete containing fresh CSH and artificially contaminated with actinides The conditions recommended by Houst (1997) should be utilized for a period of 30 days, at ambient temperature Carbonation of the surface under these conditions should be checked on non-active samples using X-ray diffraction techniques

5.2.4 Summary of concrete samples

Depending on the availability of suitable samples of contaminated RFETS buildings concrete four concrete sample types may be prepared for leaching and characterization study

1 Real actinide contaminated concrete from RFETS, for use in leaching (task 6a), and surface characterization (task 5)

2 Artificial Pu, Am and U contaminated concrete with naturally weathered surface, for use in leaching studies if RFETS concrete (1) is unavailable

3 Artificial Pu, Am and U contaminated concrete with fresh non-carbonated surface

4 Artificial Pu, Am and U contaminated concrete with actively carbonated surface

5.3 Characterization of surface contamination on RFETS concrete

Review of the open literature and of available RFETS site-specific information shows that there is a lack of knowledge of the nature and form of plutonium, americium and uranium contamination on the surface, and near surface of contaminated buildings concrete This lack of understanding leads to uncertainty in applying computational models to predict the concentration of plutonium, americium and uranium that would be released on contact of the concrete with groundwater Specifically, the identity of the plutonium, americium and uranium solubility-controlling phase is not known The actual solubility limit of these phases should be obtained from the proposed leaching experiments described above, however identification of the nature of the solubility controlling phase would add considerably to the conceptual understanding of the release of contamination This improved understanding is required to more fully predict the release of plutonium, americium and uranium over a 1,000-year period of time required, and under differing hydrogeochemical disposal designs An understanding of the nature and form of actinide contamination on the surface of concrete is important to the discussion of whether contaminated concrete behaves like contaminated soils at RFETS discussed in section 4 1

Because knowledge of the form of plutonium, americium and uranium contamination on concrete is so limited it is proposed that a preliminary characterization is performed using electron microscopy techniques to image the surface of contaminated concrete, and to perform an energy dispersive X-ray analysis (EDS) to identify areas of high contamination Such analysis should be performed in a scanning electron microscope (SEM), equipped with an automated EDS analyzer to map X-ray intensity attributed to Pu, Am and U By considering the intensity of the actinide X-ray intensity, and the presence of other cement matrix elements (Ca, Si, Al) and secondary and backscattered electron images, then conclusions could be drawn as to whether the actinide contamination is present as discrete PuO_2 grains, or as a trace component in a secondary cement phase If plutonium, americium or uranium can be clearly identified in the surface then further quantitative EDS analysis could be carried out on polished specimens Results should then be interpreted together with leach data to decide whether further characterization is warranted

It is recommended that a series of 5 samples be examined with SEM techniques with varying levels of contamination Samples should concentrate on concrete contaminated during Pu combustion Samples contaminated by Pu nitrate solution are less likely to contain discrete Pu particles Where possible some samples examined by SEM should be the same as those used in the leaching study

5.4 Leaching experiments on RFETS contaminated concrete

This section of the task plan describes the work necessary to determine leaching behavior of actinides bound to the surface of concrete The review of the available data, summarized in Section 3, has indicated that it is not possible to extract data directly from generic sources and apply them to the specific RFETS contamination scenario Therefore, a series of experiments are required to derive the relevant information

The aim of these experiments is twofold Firstly, the absolute values for leached concentrations under known RFETS conditions must be determined It is anticipated that this information would be used directly in any risk assessment process undertaken at the Rocky Flats site Secondly, the mechanisms governing leaching behavior should be established This can be fed into conceptual and mathematical models, to allow a more thorough determination of the leaching behavior of concrete bound actinides This is important, as it allows extrapolation of leaching behavior to encompass all likely conditions that may be experienced over the 1,000 year time period considered in the risk assessment process It would be impossible to encompass all possible conditions within an experimental program, and so some kind of mechanistic or phenomenological understanding is essential

5.4.1 Experimental Design

It is important to remember that the contamination bound to Rocky Flats building material is concentrated at or near to the surface of the concrete Therefore, experiments have to be designed to explore this feature This means that a traditional leaching experiment, whereby a contaminated sample is placed in a solution phase, has to be modified slightly to account for the surface nature of the contamination It is proposed that the experimental design is analogous to that employed in through-diffusion experiments (see for example, Albinsson *et al*, 1993) However, in this case the contaminant will be present on the solid phase rather than in the aqueous phase

Details of the experiments to be carried out are described in later sections However, there are a number of common features to the leaching experiments and these need to be emphasized

1 The volume of the aqueous phase must be sufficient to allow detection of radionuclides at possible low concentrations (~0 001Bq/l or 0 03 pCi/l)

2 Radionuclides to be analyzed are plutonium, americium and uranium Analysis technique should be alpha spectrometry, following chemical separation, or ICP-MS if activity levels are above 0 01 Bq/l (0 3pCi/l)

3 Experiments to be carried under closed conditions, to minimize contact with the air and evaporation

4 Experiments carried out at constant temperature, with constant agitation

5 Phase separation through ultracentrifugation followed by filtration using 30000 NMWCO (Nominal Molecular Weight cut-off) filters

6 Concentration of dissolved radionuclide monitored as a function of time

5.4.2 Task 6: Leaching of radionuclides under Rocky Flats groundwater conditions

The determination of leaching behavior of actinide contaminated concrete in contact with representative site groundwaters has to be the main emphasis of the work plan Task 6 of the Work Plan consists of leaching experiments required to derive leach rates for RFETS contaminated concrete The aims of this experimental program are

1 Determine leach behavior as a function of concrete type (fresh, weathered, carbonated),

2 Determine leach behavior as a function of contaminant concentration,

3 Determine leach behavior as a function of time

The general protocols for performing the experiments are as described above In addition, the pH should be measured at each sampling time The question of the composition of a typical Rocky Flats groundwater requires particular attention From geochemical characterization, the groundwater is described as a calcium bicarbonate dominated solution, with an associated carbon dioxide partial pressure considerably higher than atmospheric levels Therefore, the composition of typical groundwater will have to modified slightly, to be consistent with atmospheric partial pressures

5.4.2.1 Concrete Type

The literature review presented in Appendix A has revealed that the nature of the concrete surface is likely to be an important factor in determining the release of actinides In particular, the question of carbonation and extent of degradation (age) is likely to be especially crucial The question of concrete type has been discussed in Section 5 2, for the purpose of this section, it is assumed that three different concrete types are available

5.4.2.2 Contaminant Concentration

Section 3, and the results of the literature review, indicate that the concentration of contamination on the surface of the concrete will have a large influence on the leaching mechanism, and thus the concentrations leached to the groundwater Therefore, it is proposed that three different loadings of contamination (for each concrete type) are examined One of these should be above the concentration predicted to lead to solubility limited leaching behavior, while the other two should be below this value By this means, the two main mechanisms of solubility and sorption controlled leaching can be examined, and related to the extent of contamination at RFETS site

5.4.2.3 Time

The kinetics of leaching from a concrete surface is in important consideration in assessing the impact of buried concrete in contact with flowing groundwater Therefore, the experiments are to be designed such that samples are taken periodically It is proposed that the leaching experiments should be completed by 10 weeks, with five samples taken during this time However, the work schedule should allow enough flexibility to continue sampling for a time after the 10 week period, if steady state behavior is not observed, and so a time period of 15 weeks should be allowed for this eventuality The aim is to determine the time required for steady-state leaching behavior, and also, if kinetics is found to be important, to derive a rate expression

5.4.2.4 Summary

Figure 3 presents a summary of the proposed plan for Task 6 Three distinct experimental tasks can be determined

Task 6a - Leaching experiments using real RFETS contaminated concrete, or artificial contaminated concrete with naturally weathered surface Three surface contamination concentrations to be used, samples taken at periodic intervals

Task 6b - Leaching experiments using artificially contaminated concrete with fresh non-carbonated surface Three surface contamination concentrations to be used, samples taken at periodic time intervals

Task 6c - Leaching experiments using artificially contaminated concrete with actively carbonated surface Three surface contamination concentrations to be used, samples taken at periodic time intervals

Flexibility must be built into the experimental work, particularly with regard to sampling at different time periods It is clear that the findings of the first few experiments will determine the time to reach steady state, for example, and thus reduce the number of samples required in subsequent experiments

In summary, nine batch experiments are to be carried out (three different concretes, with three different concentrations of contaminants), with the aqueous phase being sampled periodically over time The experiments are scheduled to be performed over 15 weeks, with a total of 130 samples being measured through alpha spectrometry

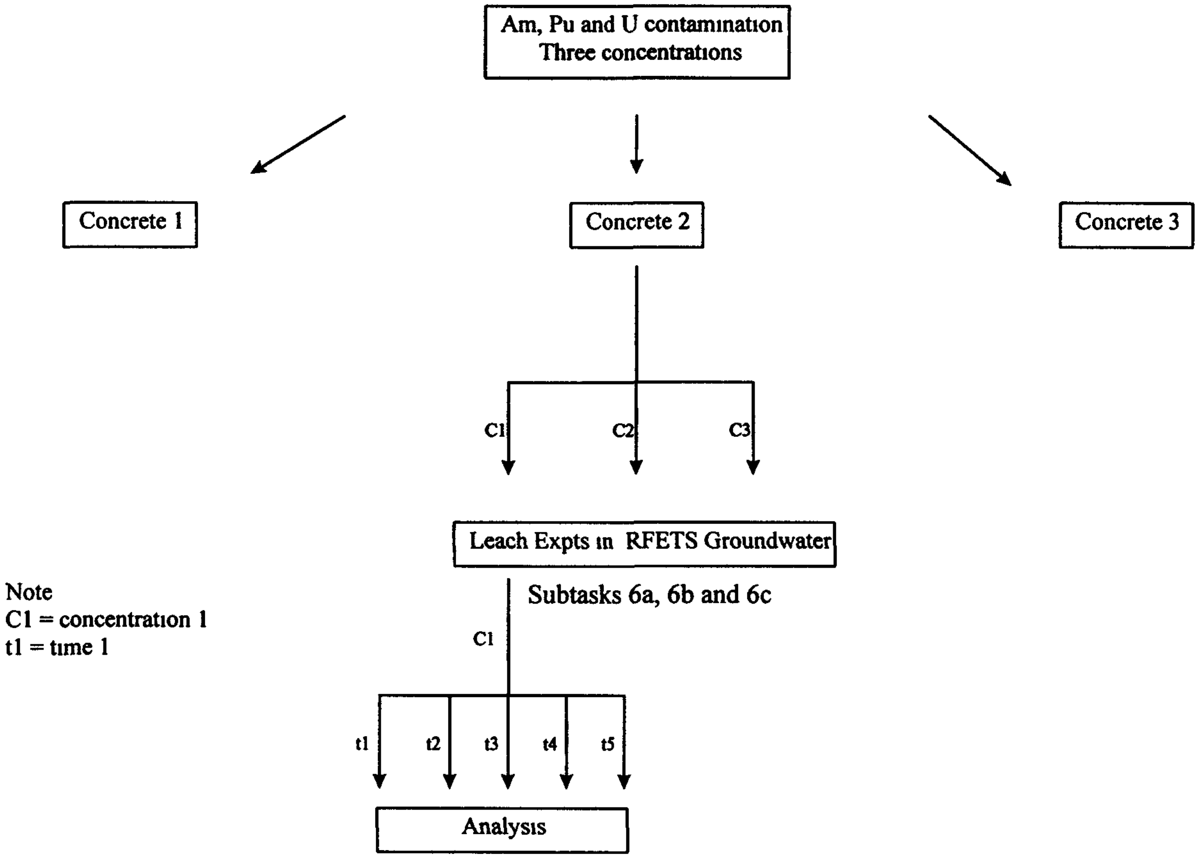

Figure 3 Summary of Task 6 Leaching of radionuclides under RFETS conditions

5.4.3 Task 7: Enhanced Leaching Experiments

In order to further investigate the leaching behavior of RFETS contaminated concrete, a series of further experiments is required The aim of these experiments is to allow extrapolation of leaching results to encompass possible variations in groundwater conditions, and also to provide guidance on the maximum amount of contaminated concrete that can be disposed, and still be protective of water quality standards

The exact details of this section of the work plan depend, to a large degree, on the results of task 6, in particular, the choice of concrete type and times for analyses It is proposed that task 7 utilize just one concrete substrate, contaminated with the same three concentrations of actinides as used previously This allows for consistency, and ease in comparison of results The main emphasis of task 7 will be to elucidate the leaching behavior of the actinides, over a range of pH's

The general experimental protocols are as described earlier, with the following additions,

1 pH adjusted to between 6 and 11 by addition of HCl or NaOH
2 Solutions analyzed for radionuclides, plus Ca, Mg, Na, Si and Al analysis by ICP-AES

A wide range of pH's is required to establish solubility controlling solids, or sorption behavior, in terms of "sorption edges" It is proposed that 12 different pH values are used, in the range indicated above Analysis of major ions is required, again, to determine solubility controlling solids, or sorption behavior

A total of 36 batch experiments are to be performed (three contaminant concentrations at 12 pH values) A total of 108 alpha spectrometry analyses are to be performed, along with 36 non-nuclide analyses using ICP-AES The duration of these experiments is again scheduled at 15 weeks

5.5 Development of a computational model to predict behavior of disposed concrete

The leaching behavior of actinides from the surface of concrete will be described by a complex combination of contributory factors Therefore, in order to determine the concentrations of plutonium, americium and uranium in concrete that are protective of water quality standards, it is important to combine all of the important chemical and physical processes into a phenomenological and, ultimately, mathematical model

The chemical processes of dissolution and adsorption have been described in earlier sections, and it is has been shown in section 4 2 how simple calculations can be used to provide an initial qualitative assessment of how the surface concentrations of plutonium, americium and uranium can be related to equivalent concentrations in a coexisting static groundwater However, the environment of buried concrete rubble will be dynamic, and so it is vital that hydrological parameters are incorporated into the model In addition, information regarding the disposed inventory of radionuclides is required

In order to provide a better assessment of the behavior of contaminated concrete at RFETS, information regarding radionuclide leach rate, solubility limits and distribution coefficients derived from the experimental work plan described in section 5 3 has to be firstly interpreted through use of models Secondly, the information has to be incorporated into a comprehensive conceptual and mathematical description of the disposal scenario Calculation of a quantitative estimate of the concentrations of plutonium, americium and uranium in concrete that are protective of water quality standards, therefore, requires this new experimental data plus a quite detailed description of the proposed disposal site, which includes the following information

- Proportion of concrete to backfill material
- Nature of backfill material, distribution coefficients, porosity
- Groundwater flow rate through the disposal facility
- Groundwater path to surface water (length, flow rate, Kd's)

A suitable computational groundwater flow model is required that includes processes of sorption, solubility and radioactive decay, and through this the chemical and hydrogeological parameters can be combined to provide an assessment and justification of the concentrations of radionuclides in concrete, and the impact on groundwater action levels

It is clear that the chemical controls on release of plutonium, americium and uranium from concrete are not the only factor to consider, and so such a computational model would provide a means to assess the design and hydrogeological features of a concrete disposal site In addition, the temporal and spatial evolution of the leaching actinides can be calculated and assessed

6. Quality Assurance Requirements

In order to ensure that the work carried out in Phase II of the investigation can be validated and, if necessary, repeated it will be necessary to exercise controls over the methods used to plan, perform and collect data arising from the experiments outlined elsewhere in this work plan

A Quality Assurance Project Plan (QAPP) written and approved before the work commences will govern these controls during the experimental phase of the work The QAPP will ensure that the data collection process is defined, controlled to the extent required, verified and documented The design process for these controls will identify all relevant activities pertaining to environmental data operations, establish performance specifications, and identify appropriate controls Planning for the management of data arising from the proposed work will be performed using the Data Quality Objectives (DQO) Process This Process is a series of steps designed to establish criteria for data quality and for developing experimental data collection designs (NUREG) Use of the DQO Process will improve experimental effectiveness and efficiency The Process uses a graded approach to data quality requirements and is usually carried out early in the experimental process design and provides input into the QAPP regarding environmental data management DQOs are qualitative and quantitative statements, which can

- Clarify the experimental program objective
- Define the most appropriate type of data to collect
- Determine the most appropriate conditions for collecting the data
- Specify limits on decision errors that will be used as the basis for establishing the quantity and quality of data needed to support the decision

The DQO Process is iterative and ensures that planning is performed properly the first time and established performance measures for the data collector are appropriate For the experimental work described in this work plan, the use of the DQO Process and outputs will form an integral part of the QAPP

Overall, the design of the QAPP shall ensure (but not be limited to) consideration and development of detailed specifications for

- Assessments needed during the project (e g surveillance, audits)
- The receipt and control of radioactive materials including, but not limited to
- Logging in of materials
- Assignment of identification numbers

- Safe storage
- Packaging, shipping and custody
- Handling and usage of radioactive materials
- Protection of worker and public health and safety
- Data verification and validation methods
- Data reporting requirements
- Integration cost or schedule constraints into the design
- Calibration and performance evaluation of testing equipment
- Selected analysis of duplicates, blanks and surrogate samples
- Controlling non-conformances
- Readiness reviews prior to data collection
- Requirements and qualifications for sampling and analysis personnel
- Sample types, numbers and quantities, and sampling location requirements
- Selection of analytical methods and their quality performance expectations
- Measures for the disposal or minimizing procedures for wastes produced during sampling and analysis operations

The process shall ensure that the data generated are traceable to the procedures used to produce the data and to the personnel generating or collecting the data Data transfer, reduction, verification and validation requirements must be determined and documented The requirement for necessary reports to management for status of the work, interim results, and the results of assessment activities shall be identified and documented Any restrictions to be imposed on the use of the generated data will be clearly defined

The QAPP will encompass the above requirements and the document will be reviewed and approved by a technically competent designated person(s) before use The QAPP will be subject to regular review by a technically competent person at regular defined intervals during the period of performance

These specifications will be in the form of QA Procedures which, when followed, will ensure that QA requirements for the experimental work are met and maintained The principal text, which defines many of the above listed requirements, is Quality Systems Requirements For Environmental programs ANSI/ASQC E4-1993

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7. Performance Budget and Schedule for Phase II work

Figure 4 outlines a schedule to undertake the work plan described in this report Tasks relating to the study of samples of RFETS contaminated concrete have been listed separately The duration of task 2 relating to the selection, sampling and shipment of RFETS samples cannot easily be estimated by this review The schedule shown in Figure 4 assumes that information regarding sample types, locations and contaminant concentrations is known when the Notice to Proceed is issued This will allow sample selection and preparation of a sampling plan (SAP) to be undertaken immediately Any additional surveying of the RFETS site will obviously push back the proposed start date of subsequent tasks If task 2, overall, extends more than 3 months it will be critical to the completion of the project within the timescales indicated in Figure 4 If samples of RFETS contaminated concrete are unavailable, Task 2 and Task 5 would not be required Time durations listed in Figure 4 represent actual duration (e g experiment duration) rather than man weeks worked

The overall budget for this work plan is estimated to be in the region of $160 5k And again, it should be noted that this budget figure excludes all costs incurred in task 2 associated with the selection, sampling and transport of samples of RFETS contaminated concrete A breakdown of the estimated budget by task is shown in Table 4 Laboratory based tasks include staff, analysis, equipment and overheads costs

[illegible]	[illegible]	[illegible]
1	RFETS Sample Availability	-
2	Select RFETS Samples	7,000
3	Prepare Artificial Samples	7,500
4	Artificial Carbonation	6,000
5	Surface Characterization	5,000
6	Leaching Experiments	46,000
7	Enhanced Leaching Experiments	28,000
8	Model Development	16,000
9	Interpretation and Reporting	15,000
	Project Management and QA	30,000
Total		**160,500**

Table 4 Breakdown of the Performance Budget, by task

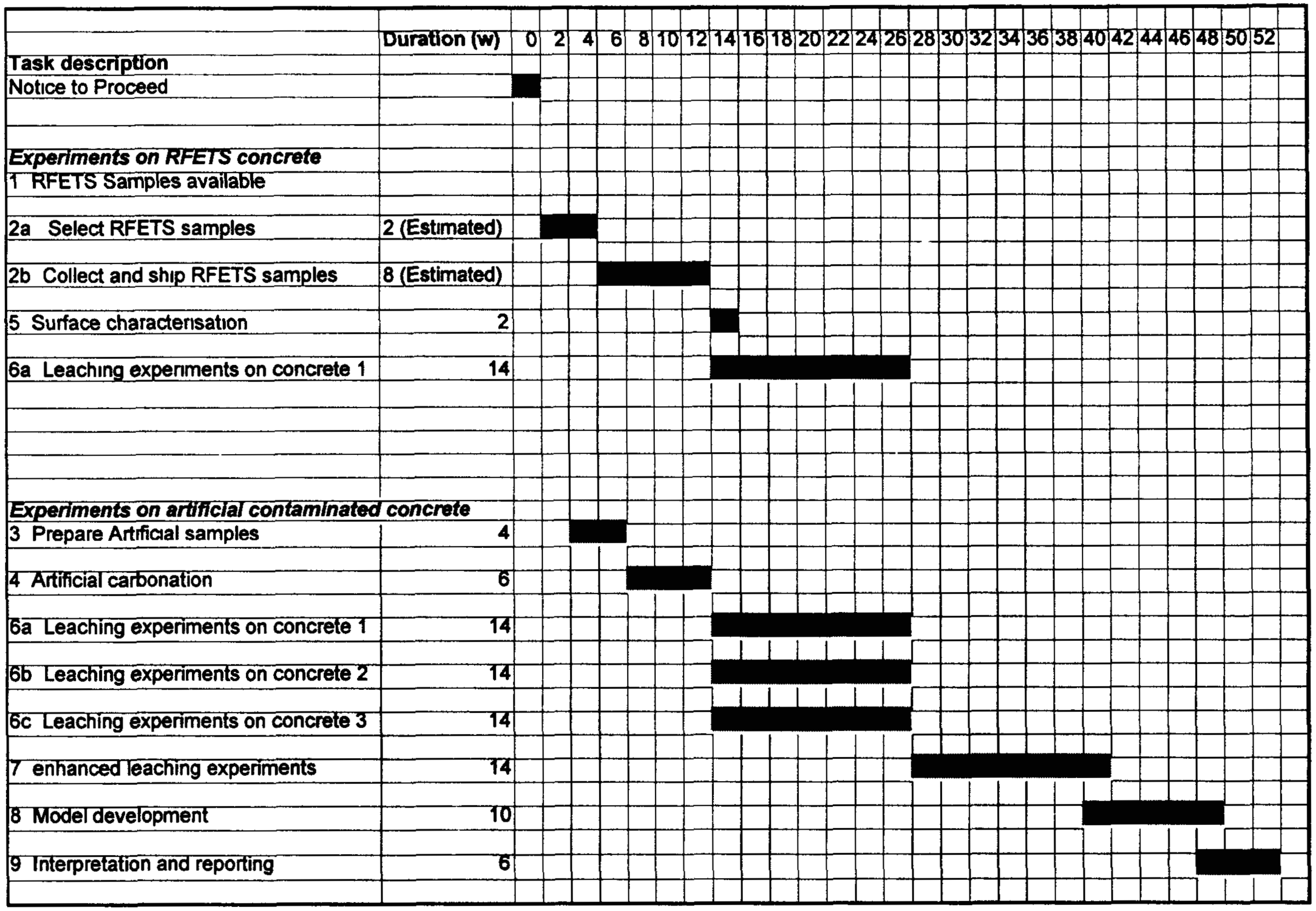

Figure 4 Work plan schedule

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9. List of Acronyms, Abbreviations and Symbols

DOE	U S Department of Energy
M	Molality, moles per kilogram of water
mg/l	milligrams per liter
pCi/l	picocuries per liter
RFETS	Rocky Flats Environmental Technology Site
RFCA	Rocky Flats Cleanup Agreement
SEM	Scanning Electron Microscopy
K_d	Equilibrium distribution coefficient, representing extent of sorption onto a solid surface Defined as the ratio of concentration sorbed against concentration in the aqueous phase Units are volume/mass (e g m^3/kg, L/kg)
R_d	As K_d but more accurately used to describe empirically measured distribution coefficients, where thermodynamic equilibrium is not necessarily true
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
CSH	Calcium Silicate Hydrate (cement mineral phase)
Bq/l	Radioactive events per second per liter
MCL	Maximum Concentration Levels
QAP	Quality Assurance Plan
DCF	Dose conversion factor

10. Appendix A

Appendix A:

Literature Review on Behavior of Contaminated Concrete Over Time and Relevance to Plutonium, Americium and Uranium Contamination at The Rocky Flats Environmental Technology Site

Contents

1. Summary

This Appendix provides a review of current literature on the behavior of plutonium, uranium and americium in contaminated concrete with relevance to surface contaminated concrete at the Rocky Flats Environmental Technology Site (RFETS) This review is used as a basis to design a draft work plan to more fully understand the mobility of this contamination at RFETS for the purpose of assessing radiologic risk over a period of 1000 years The aim of the overall project is to provide a comparison of the behavior of plutonium, uranium and americium present in contaminated concrete to that present in soils for which risk criteria are defined The project will also establish what concentration of these radionuclides can be bound in concrete at RFETS that will be protective of water quality standards

A review of literature on cement and concrete degradation, radionuclide leaching from cement and concrete, and plutonium, uranium and americium solubility and sorption under cementitious conditions has been undertaken Sufficient information is available in the literature and in the RFETS Sitewide Geoscience Characterization study to qualitatively predict the degradation behavior of concrete rubble at RFETS and to provide background information for evaluating the chemical controls on leaching, solubility and sorption of plutonium, uranium and americium The main process of degradation affecting the predominant surface contamination of RFETS concrete is likely to be carbonation, the reaction with carbon dioxide either in soil gases or dissolved in groundwater Attack by sulfate and processes controlled by microbial activity may also be relevant, but the involvement of these processes is more uncertain at present Corrosion of steel rebar is also likely to contribute to the cracking of concrete blocks The main form of degradation by carbonation is unlikely to result in dissaggregation of the surface and may in fact result in a more resistant surface that is less prone to freeze-thaw and mechanical erosion Formation of silica and iron hydroxide colloids is possible during degradation that could influence the migration of actinides

Carbonation of the surface zone containing plutonium, uranium and americium contamination has important implications for the chemical controlled leaching of radionuclides The local fluid pH surrounding the contamination will be lowered from above 12 to ~ 8 by carbonation Redox (Eh) condition will be unaffected by carbonation and may not be changed from that of the background geochemistry, steel corrosion is the only likely mechanism by which reducing conditions may be established It is emphasized that these conditions are not typical of the extreme high pH, low Eh deliberately engineered in radioactive waste repository designs and thus plutonium, uranium and americium are likely to be more mobile in RFETS concrete than in such repositories

Experimental studies of leaching of plutonium, uranium and americium from cementitious materials are very limited This is largely a result of the low mobility of actinides under these conditions, and the need for long time scale experiments Data that is available would confirm the proposition that liquid contamination as well as particulate contamination is very close to the surface Under these circumstances diffusive control is less important as the contamination will be in close contact with groundwater Leaching from surface contamination is considered to be controlled by processes of sorption onto the degraded cement surface and, where concentrations are sufficiently high, by solubility control from a solid contaminant (e g PuO_2) In view of this, a review of literature on plutonium, uranium and americium solubility and sorption under conditions in

the degraded concrete surface has been undertaken A substantial amount of literature is available concerning the solubility of actinides under cementitious conditions, although the majority of these studies are concerned with higher pH's than relevant here, a good understanding of the controls on solubility and sorption is possible An important factor controlling solubility, and hence release is the nature and solubility of the actinide contamination Sorption distribution coefficients (Rds or Kds) for actinides under high pH conditions are quite well defined, but again these mainly relate to high pH, non-carbonated cement substrates Actinide sorption is generally less effective at lower pH, and uncertainties exist in the sorption mechanism on carbonated cements and on the uptake of contaminants by calcium carbonate

In summary, a reasonable understanding of the degradation of concrete at RFETS is possible, the question of the mobility of plutonium, uranium and americium under the chemical conditions established in the degraded concrete is more uncertain These contaminants are likely to be solubility controlled in the very near surface of the degraded concrete, however the nature and solubility limit of the solid contaminant phases are unknown

2. Introduction

This Appendix comprises a review of the literature on processes relevant to the mobility of the radionuclides plutonium, uranium and americium present in contaminated concrete present at the Rocky Flats Environmental Technology site (RFETS) It has been suggested, for the purposes of assessing radiological risk, that release of radionuclides from contaminated concrete rubble remaining after decommissioning activities at RFETS will be similar to that from release from soil over a 1,000 year period (RMRS, 1998) On this basis a possible radiation dose based standard for determining the concentration of contaminants in concrete is the Tier I soil action level defined in the Rocky Flats Cleanup Agreement (RFCA) (DOE, 1998) Another possible standard is that radionuclides leached from concrete will be protective of water quality defined by Tier II action levels for ground water, Pu, Am 15pCi/L , U 100pCi/L (DOE, 1998, Attachment 5)

The aims of this project as defined in the statement of work (RMRS, 1998) is to provide a qualitative assessment of the physical and chemical properties of plutonium, americium and uranium contamination in concrete and to answer the questions

"Does concrete behave like soils at RFETS over the 1,000 year assessment period?"

"What concentration of plutonium, americium and uranium may be bound in concrete left at RFETS after decommissioning that will be protective of water quality standards?"

This literature review is the first stage of this exercise, the objectives of the review are to provide a preliminary understanding of the processes involved in concrete degradation and plutonium, americium and uranium leaching from concrete, at RFETS This review includes examination of site-specific data provided principally in the Groundwater Geochemistry Report for the RFETS (EG&G, 1995), together with verbal descriptions of the nature of the contamination in concrete from RMRS and Kaiser-Hill staff A qualitative description of the degradation of concrete at RFETS and the chemical factors governing the mobility of plutonium, americium and uranium are provided Comments are made on current inadequacies in the open literature in understanding processes of actinide mobility from contaminated concrete at RFETS

2.1 Overview of radionuclide/cement literature

An extensive amount of literature exists in peer-reviewed journals, conference proceedings and in reports of various agencies and research institutes on the application of cement and concrete to the disposal of radioactive waste Cement-based materials are used commonly for the encapsulation of low- and intermediate-level waste and for proposed backfill material in repository designs Concrete is used extensively in the structural design of radioactive waste repositories Cement and concrete form a low permeability barrier to the ingress of groundwater to radioactive waste In addition, the high pH and high surface area of the cement matrix provides a chemical barrier to radionuclides, providing retardation by sorption and lowering solubility To understand the behavior of this chemical barrier extensive research has been carried out to predict the evolution of chemical conditions in cement pore water over very long periods of time (100,000 years) Much of this research has concentrated on predicting pH during leaching of cement by groundwater as this is an important parameter controlling both the solubility and sorption of radionuclides Other areas of cement degradation, which impact on the structural integrity of concrete are attack by chloride, sulfate and magnesium, which can be at high concentrations in deep subsurface brines The microbial promoted attack of concrete is also quite frequently discussed in the radioactive waste literature

Measurement of leaching rate of certain radionuclides from cement wasteforms has been carried out Quite extensive experimental studies have been made of Cs, Co, Sr, I, C leaching(Amoya and Suzuki, 1992, Krishnamoorthy et al, 1992, Plecas et al, 1992b, Miyamoto et al, 1993, Nishi et al, 1991, Kato et al, 1996, Peric et al, 1993, 1994, 1995) and models based on diffusive transport of these relatively mobile elements have been developed (Plecas et al 1992a, Kim et al, 1992, 1993, 1996) Such data and models are not particularly relevant to the leaching of contaminants from RFETS concrete, here the contamination is in the form of Pu, Am and U, and the surficial nature of the contamination will not be influenced by diffusive properties of the cement matrix

Studies of the leaching of actinides from cementitious materials are much more limited, this in part reflects the very low mobility of actinides in cementitious systems, with the consequence that experimental time scales have to be extremely long In addition, the focus of this limited work has been concerned with the leaching of radionuclides from cement-encapsulated waste, rather than surface contamination Diffusion measurements do however provide a useful indicator of the depth to which actinides can penetrate into concrete

Despite the lack of data explicitly dealing with actinide leaching from concrete, there is another avenue to be explored Due to the use and proposed use of cementitious material for the immobilization of radioactive waste, properties of radionuclides in cement environments have been extensively studied Thus solubilities of actinides in cement leachates have been determined, and sorption onto cement pastes have been measured Although these do not, on the face of it, appear to be directly relevant to RFETS leach behavior, these experiments may in fact reveal useful information about the leaching of radionuclides from cements

As a consequence of the literature search criteria used, and the number of references related to radioactive waste disposal, many references examined relate to the use of cement based materials in repository designs and waste encapsulation It should perhaps be emphasized at this stage that although the literature reviewed is sourced largely from such repository studies, the processes controlling plutonium, americium and uranium mobility at RFETS are not typical of those in radioactive waste repositories In particular

- Contamination in RFETS concrete is surficial and will be in close contact with groundwater
- pH will be significantly lower than in engineered repositories, where it forms an integral part of the multi-barrier approach

2.2 Literature search criteria

The literature search was carried out using BNFL's Information Retrieval Service The following databases were searched

BIOSIS Previews	CA SEARCH (Chemical Abstracts)
CAB ABSTRACTS	Ceramic Abstracts
Chemical Engineering and Biotechnology Abstracts	Derwent World Patents Index
DIALOG SourceOne Engineering	Dissertation Abstracts Online
Ei Compendex Plus	Electric Power Database
EMBASE	Energy, Science and Technology (DOE)
Enviroline	FLUIDEX
GeoArchive	GEOBASE
GeoRef	Inside conferences
INSPEC	JICST - Eplus
Life Sciences Collection	METADEX
NTIS	Nuclear Science Abstracts
PASCAL	SciSearch
SPIN	TOXLINE
TRIS	Wilson Applied Science
World Translations Index	

The following keyword searches were made

1 Cement or concrete and leach and radionuclide (192 returns)
2 Cement or concrete and degradation (156 returns)
3 Concrete and contamination and radionuclides or uranium or plutonium or fission product or nuclear waste or radioactive waste (95 returns)

These searches were selected so that the key publications on radionuclide mobility in cementitious radioactive waste systems would be covered, the relevance of these publications was determined as site specific data was received from RMRS The last search concerning concrete contamination was the least successful and references here mainly concerned decontamination methods, contamination associated with nuclear reactors and nuclear fall out On the basis of document title and available abstracts 60 papers and documents were chosen as being relevant and were obtained from the British Lending Library In addition to these references a number of other sources of literature were examined which included

1 Materials Research Society Symposia " Scientific Basis for Nuclear Waste Management" VIII-XXI (1985-1998)
2 A collection of references on actinide solubility and sorption

In addition reference lists in reviewed publications were examined for further relevant references A list of all references used in this review is provided in the Bibliography

3. Nature of Contamination of Rocky Flats Concrete

Information regarding the nature of contamination of construction concrete at RFETS is limited and no documented descriptions were available Verbal descriptions of the nature of the contamination were provided at two meetings (Roberts, personal communication, Ervin, personal communication) Contamination of RFETS construction concrete by Pu, U and Am is thought to be present in three forms

- Surface contamination of very fine-grained PuO_2 with associated Am and U from a plutonium fire
- Contamination from Pu nitrate solution seepage through concrete
- Uranium present in locally derived aggregate used in concrete

The surface contaminated Pu is thought to be the most important for discussion here since contamination by Pu nitrate may be at levels too high for in-situ disposal Plutonium is likely to be present in the chemically stable form PuO_2, as very fine-grained smoke particles resulting from combustion of Pu metal (Baldwin and Navratil, 1983) Surface deposited PuO_2 particulates in concrete are generally likely to be limited to the first few millimeters (DOE, 1995) Uranium and americium are assumed to be present on the surface in a similar form to surficial Pu, although the nature of these compounds is more uncertain than for plutonium, uranium could be present as either UO_2 or in the U(VI) oxidation state as hydrated phases (e g schoepite) if contamination is related to combustion, americium may be present as hydroxide The depth of liquid nitrate contamination on RFETS concrete is not known Experiments have however been performed on the attenuation of Pu and Am mobility in concrete immersed in nitrate (Jakubick, 1987) which show that at a steady state uptake from 10^{-5} M Pu and 10^{-6} M Am solutions both Pu and Am penetrated to a depth of around 2cm in concrete pre-treated with 3M nitric acid Pu diffusion and leaching experiments reviewed in a later section indicate that diffusion is extremely slow Liquid Pu nitrate contamination is therefore likely to be close to the surface, and thus will be influenced by chemical degradation of the concrete Uranium in aggregate is present presumably at background levels in local bedrock Uranium in aggregate is assumed to be evenly distributed through the concrete and its release will be controlled by the gross degradation of the concrete

4. Site Specific Geochemistry

The geochemistry and composition of the groundwater at RFETS is a crucial factor in determining the leaching behavior of surface contaminated concrete Therefore, a review of the groundwater geochemistry is appropriate This review is based on the comprehensive site characterization report (EG+G, 1995), and it has not be deemed necessary to offer any new interpretation Rather, those factors of groundwater geochemistry that are important, from a concrete leaching context, have been highlighted, extracted and assessed The aim is to summarize the magnitude and variation of important parameters, in order for the literature review to be placed within a site-specific context

4.1 Summary of Rocky Flats Geochemistry

The hydrology of the RFETS site is divided into two distinct units, the Upper Hydrostratigraphic Unit (UHSU) and the Lower Hydrostratigraphic Unit (LHSU) The UHSU is composed of unconsolidated, surficial deposits and weathered sandstone of the underlying Laramie and Arapahoe formations The LHSU consists of the unweathered portions of the Arapahoe and Laramie formations

Groundwater flow is generally from west to east, with permeability and hydraulic conductivities greater in the UHSU than in the LHSU There appears to be limited hydrological communication between the two units The vertical hydraulic conductivity of the LHSU is an order of magnitude less than the horizontal conductivity, indicating that the LHSU acts as a hydraulic barrier to vertical groundwater flow
The groundwater geochemistry report (EG+G, 1995) presents data from samples collected from 1990 and 1994, from 532 wells The data is presented in terms of Stiff and Piper diagrams, and time series graphs In addition, the results from geochemical modelling (using WATEQF) and inverse modelling/reaction path modelling (using NETPATH) are also shown and discussed

In summary, the UHSU and LHSU comprise significant geochemical units, with the former predominantly calcium bicarbonate dominated and the latter considerably more varied, ranging from a sodium bicarbonate to sodium sulfate dominated groundwater A major exception to these generalities is found in groundwaters close to the Operational Units, where contamination results in UHSU compositions as varied as LHSU waters, with sodium and sulfate particularly enhanced

Data from wells along four proposed flow paths are also presented, and also interpreted through modelling In general, the concentrations of major cations (Ca, Mg, Na and K) and total dissolved solids increase along the flow paths, which could be indicative of contamination, infiltration or mixing of groundwaters However, inverse modelling suggests that the evolution of groundwater composition can be explained by natural geochemical reactions, such as dissolution and precipitation of mineral phases, and ion exchange reactions In particular, the precipitation of kaolinite, SiO_2 and iron minerals, the dissolution of calcite, pyrite, microcline and chlorite and exchange of calcium for sodium, would appear to be the more important mechanisms The conclusion is that the mixing of additional groundwaters is not required to account for the evolution of major element geochemistry along the major flow paths

However, local variations are shown to exist, particular along the Industrial Area flow path, where the major ion composition of the UHSU changes from a calcium bicarbonate water to a mixed sodium bicarbonate/sodium sulfate groundwater In particular, groundwaters close to the Solar Evaporation Ponds indicate elevated levels of major cations, strontium, uranium-235, chloride and sulfate, while groundwaters close to the Landfill exhibit low pH's, potentially low Eh and elevated metal concentrations It does not appear that these local variations are reflected in the overall geochemical evolution along the flow paths, as the groundwater at the end of the flow path is again a calcium bicarbonate water

4.2 Variations in Specific Parameters

4.2.1 Carbonate

Carbonation is an important degradation mechanism, which affects the physical and chemical integrity of concrete Carbonate also affects the solubility and sorption of actinides in groundwater As has been mentioned above, the groundwaters of the UHSU can be classified as calcium bicarbonate, with the carbonate level likely to be controlled by calcite solubility Taking data from the Flow Path diagrams (Figures 5-8 to 5-17, EG+G, 1995), bicarbonate concentrations appear to vary from less than 1 mg/l in the background wells of the Southern Flow Path to 200 mg/l along the Woman Creek flow path However, boreholes in the Industrial area exhibit concentrations much higher than this For example the Stiff diagrams presented in Plate 2 (EG+G, 1995) show bicarbonate concentrations of 20 meq/l (equivalent to 1200 mg/l)

The Lower Hydrostratigraphic Unit exhibits lower bicarbonate levels, as shown in Figure 6-46 (EG+G, 1995), where a uniform concentration of 100 - 200 mg/l is observed site wide, apart from area around the Industrial Area, where concentrations rise to above 200 mg/l

4.2.2 Sulfate

Sulfate is an important anion producing enhanced degradation of concrete Sulfate is also a potential microbial substrate, which could enhance concrete degradation and radionuclide mobility Sulfate is generally low in the UHSU, typically less than 10 mg/l in the Woman Creek Flow Path background wells In the Industrial area sulfate is much more variable increasing to over 1000 mg/l The groundwater around the Solar Evaporation Ponds and Ponds B along the Walnut Creek appear to be particularly enhanced with respect to sulfate concentrations

Figure 6-51 (EG+G, 1995) indicates that the concentration of sulfate in the LHSU is fairly constant across the site, less than 100 mg/l This may indicate that the background concentrations of sulfate are slightly higher in the LHSU than in the UHSU There are increases in the Industrial Area, but these do not appear to be as high as those in the UHSU

4.2.3 Chloride

Chloride produces enhanced degradation of concrete and induces corrosion of steel reinforcements (rebars) Chloride generally behaves like the other major elements, as concentration tends to increase along the flow paths In the UHSU, background concentrations are less that 25 mg/l, while the concentrations at the RFETS plant are generally between 25 and 50 mg/l, with hot spots, again, around the industrial area (where concentrations exceed 500 mg/l in places) In the LHSU, concentration is fairly uniform at less than 50 mg/l

4.2.4 Reduced Nitrogen, Sulphur and Organic Matter

Reduced species are required for microbial degradation, and nitrogen, sulphur and carbon are often present as reduced species in soils and groundwater There is no mention of reduced nitrogen, in the form of ammonium, in any of the groundwater analyses, which is reflected in the redox measurements (see later) Pyrite is present in certain areas of the site, and this would appear to be only source of sulfide Organic composition is less clear, and apart from anthropogenic organic compounds, the presence of organics is not mentioned

4.2.5 pH

pH is an important control on radionuclide mobility, and on alkali and Ca leaching of concrete The background pH at the RFETS appears to be between 7 5 and 8, and appears to be fairly constant along all four flow paths, no doubt due to calcite equilibrium The highest pH's occur around the Industrial Area, where the pH reaches values above 8 Groundwater close to the Landfill exhibits relatively low PHS (below 7) In general, there is relatively little pH variation over the site, in the UHSU The isoconcentration map for the LHSU does indicate three area where the pH is above 10 However, these appear to be isolated and the pH is otherwise below 8

4.2.6 Redox

The oxidation state of redox sensitive elements such as plutonium and uranium is important to their mobility Redox measurements can also give an indication of the extent of microbial activity The amount of redox data available from the site is sparse, and the difficulties in measuring Eh is acknowledged The redox potentials were measured using a flow-through cell, and the resulting Eh's are in the range of 0 09 to 0 32 V i e mildly oxidizing The presence of siderite and pyrite suggests reducing conditions, thus either there are pockets of anaerobic waters or, more likely, the presence of these minerals is indicative of the conditions in the past when these minerals were formed It is mentioned that potentially low Eh's may be encountered close to the Landfill, but the values are not presented in the report

5. Cement and Concrete Degradation

5.1 Introduction

Several physical, chemical and biological processes contribute to the degradation of cement and concrete (Lagerblad and Tragardh, 1996, Glasser, 1997, Rogers, 1993a) Many of the processes are inter dependant and involve some aspect of chemical degradation Chemical degradation reactions of cement minerals are important as they control the local pore fluid chemistry where radionuclide contamination may exist Fluid chemistry exerts a strong influence on the solubility of the actinides and in some cases radionuclides may co-precipitate with cement alteration products Sorption of radionuclides is also influenced by fluid chemical conditions such as pH as well as the surface mineralogy It is therefore necessary to review the major chemical reactions involved in cement and concrete degradation

The main chemical processes affecting cement and concrete are

- Leaching and acid attack
- Carbonation
- Sulfate, magnesium and chloride attack
- Alkali-aggregate reactions
- Corrosion of steel rebars

Biodeterioration of concrete principally involving microbial induced attack facilitates localized chemical degradation by several processes leading to enhanced surface degradation of concrete Since contamination in RFETS concrete is concentrated at the surface such processes operating at the groundwater interface must be considered to be potentially important in releasing radionuclides

The mobility of radionuclides in groundwater can be enhanced by the presence of suspended particulate colloidal materials onto which radionuclides may be sorbed Since concrete degradation may produce such fine-grained material available literature on colloid generation is considered

An understanding of long-term degradation of concrete can be obtained from study of ancient analogues of modern concretes and from computer models Computer models include prediction of the structural evolution of concrete repositories and the prediction of chemical degradation and pH evolution Analogues and models provide an estimate of the time-scale of concrete degradation and the likely extent of degradation during the 1000 year assessment period

Following review of the above aspects of cement and concrete degradation the processes most relevant to RFETS will be discussed with consideration to the nature of radionuclide contamination and site-specific groundwater conditions

5.2 Chemical evolution of cement minerals

Hydration of Portland Cement (OPC) leads to the formation of a variety of chemical phases which make up hardened cement (Lea, 1980) The initial pore solutions formed on dissolving anhydrous OPC are strongly oversaturated and hydrated silicate phases form in equilibrium with the pore solution The kinetics of hydrated OPC mineral formation is however slow, initial phases formed are amorphous gels which form more crystalline phases with accelerated ageing, and at increased temperature The compositions of the initial gel hydration phases formed are variable and the sequence in which they form is partly dependent on temperature and curing conditions During leaching by pure water, alkalis and calcium are removed from the cement minerals which results in a decrease in pH of the cement pore fluid and change in composition of the cement matrix

5.2.1 Hydrated cement minerals

A standard nomenclature is used to abbreviate OPC and hydrated cement mineral formulae in most publications on cement and concrete

Abbreviation	Oxide Formula
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
s	SO_3
H	H_2O

The symbols **m** and **t** are commonly used to denote the ratio of calcium in a mineral and correspond to mono- and tri- respectively e g monosulphate AFm

Some of the main hydration products are

- Calcium-silicate-hydrate (CSH) - the main component of hydrated OPC Amorphous to semi-crystalline with Ca/Si molar ratio of 0 8 to 3 0, with variable water content CSH forms during the hydration of anhydrous tri- or di- calcium silicate with water yielding $Ca(OH)_2$ and a more silica rich CSH
- Calcium hydroxide - a crystalline product forming large crystals
- Aluminium-iron-mono (AFm) these phases have the general formula $(Ca_2(Al, Fe) (OH)_6xXyH_2O$, where X is an equivalent of a single charged anion Monosulphate and Friedels's salt are important hydrated cement phases containing sulfate and chloride respectively
- Tri-calcium-aluminates (AFt) formed by hydration of calcium aluminate, these phases can contain anions such as SO_4^- and CO_3^- The sulfate mineral ettringite is an important member of this group, resulting in sulfate promoted degradation
- Hydrogarnet - a solid solution series containing Ca, Si and Al, which coexist with CSH phases
- Brucite ($Mg(OH)_2$) small amounts of this phase are present in hydrated cement Secondary brucite is responsible for Mg promoted attack

In pure OPC based concretes with low concentrations of reactive alumina, calcium hydroxide and CSH are the main phases present Alumina containing phases are more important to applications of cement grouts and backfills used in the encapsulation of radioactive waste which include blast furnace slag and pulverized fly ash as additives, such materials contain a high content of pozzolanic reactive alumina which results in the formation of aluminous hydrated cement phases Aggregate added to concrete may contain alumina in the form of rock forming minerals, however, these phases are largely unreactive

5.2.2 Leaching of $Ca(OH)_2$ and CSH

Extensive experimental studies have been performed examining the leaching of $Ca(OH)_2$ and CSH in pure water (Berner, 1987, Adenot *et al*, 1992, Atkins *et al*, 1992a,b,c, 1994, Engkvist *et al*, 1996, Delagrave *et al*, 1997, Glasser, 1997, Bennett *et al*, 1992, Pfingsten and Shiotsuki, 1998, Duerden *et al*, 1997, Neall, 1996, Quillin *et al*, 1994) The majority of these studies have been performed to examine the pH behavior during leaching which is an important control on the mobility of radionuclides from cement-based grouts and backfill materials The leaching of OPC based cements can be divided into five main periods (Figure 1)

- Flushing of residual alkalis (NaOH and KOH) from pore spaces at pH 12-14
- Leaching in the presence of $Ca(OH)_2$ pH is buffered at over 12 0, CSH co-existing with $Ca(OH)_2$ has a Ca/Si ratio of approximately 1 8
- When $Ca(OH)_2$ is exhausted pH is controlled by the CSH phase which dissolves incongruently, preferentially releasing Ca into solution pH decreases from over 12 0 to ~10 5 as CSH changes in composition from Ca/Si ratio 1 8 to 0 8
- On reaching a Ca/Si ratio of ~0 8 CSH dissolves congruently and pH remains constant at ~10 5 until the CSH finally dissolves
- Following dissolution of CSH pH is controlled by secondary Ca minerals, typically calcite under groundwater conditions pH drops to ~ 7-8 dependent on carbonate levels in the groundwater

The duration of these pH buffers depends on the amount of each mineral in the concrete, the permeability (related to the quality of the concrete), and the groundwater chemical composition The effect of alkalis is relatively short-lived since these are present in the initial porespace and are removed after flushing of 2-3 pore volumes The amount of free $Ca(OH)_2$ is determined by the amount of pozzalanic material present in the concrete, excess $Ca(OH)_2$ reacts with such material forming CSH and CASH phases Pure OPC concretes used for construction purposes, which do not contain blast furnace slag or pulverized fuel ash will contain significant amounts of free $Ca(OH)_2$ CSH form the main buffering phase, the rate and duration of dissolution of Ca depend on temperature, surface area and the concentration of Ca, Si and carbonate in the groundwater Dissolution is most rapid in soft CO_2 -rich water, and slower in $CaCO_3$ waters Acidic water produced by microbial action, such as sulfide oxidation, or acidic spillage onto concrete will effectively accelerate the leaching process Under accelerated acidic leaching diffusion processes limit the leaching process (Lefebvre, 1997) The sequence of changes in cement mineralogy occurring during leaching illustrated in Figure 1 can be considered to occur either as function of time, or fluid volume at a given point, or as function of distance representing zoned alteration of a concrete surface

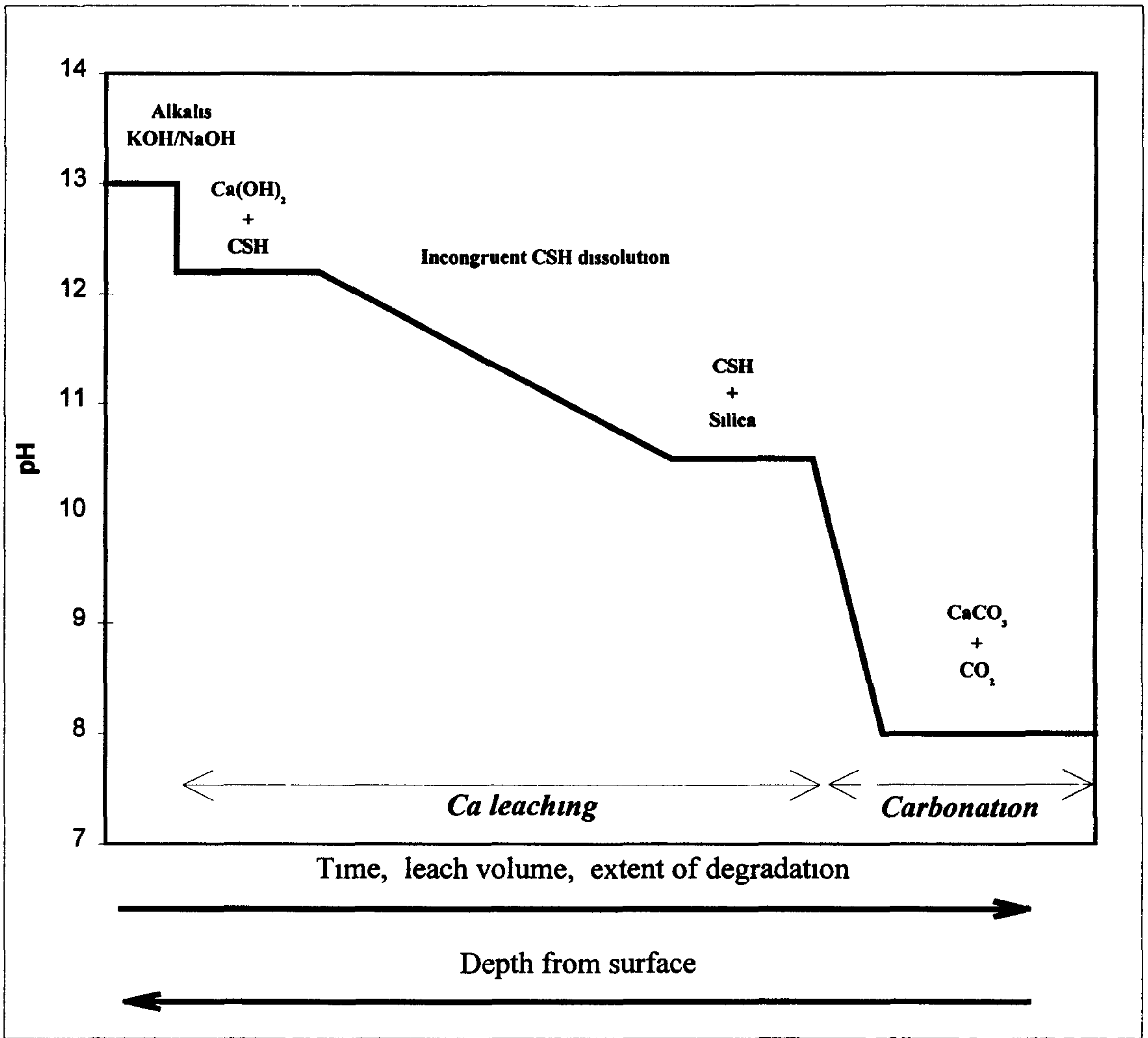

Figure 1 Evolution of cement pore fluid pH during leaching

5.3 Carbonation

Carbon dioxide reacts strongly with the alkaline components of OPC concrete during the process of carbonation Both $Ca(OH)_2$ and CSH react with CO_2 to form calcite

$$Ca(OH)_{2\,(s)} + CO_{2\,(g)} = CaCO_{3(s)} + H_2O$$

$$CSH_{\,(s)} + CO_{2\,(g)} = CaCO_{3(s)} + SiO_{2(s)} + H_2O$$

Carbonation can occur in both saturated groundwater, in the unsaturated zone, and in above ground structures In soils carbonation is favored by high CO_2 content and the humidity of the soil gas Optimum humidities are around 75%RH (Houst,1997), the carbonation reactions only occur in the presence of water, however water produced by carbonation must be allowed to diffuse out of the carbonated layer Cement permeability and original water/cement ratio are therefore important to the extent of carbonation Tuutti (1982) has investigated the effects of permeability on carbonation (Figure 2), in rainwater a good quality concrete with W/C 0 45 will carbonate to a depth of 5mm in 50 years In groundwater where CO_2 levels are higher than in the atmosphere, carbonation will be more effective (Lagerblad & Tragardh, 1996)

Formation of calcite from $Ca(OH)_2$ results in an increase in volume of 12% (Houst, 1997) which reduces porosity Despite a decrease in porosity overall shrinkage occurs (Houst, 1997) and microcracks develop (Walton *et al,* 1997) Decreases in porosity are beneficial in view of degradation by freeze-thaw mechanisms Overall the durability of cement increases during carbonation Carbonation results in a large decrease in pH to ~8, where steel reinforcement is more prone to corrosion and where microbial induced degradation may become established Studies of contaminant leaching from carbonated cements show varied behavior, some contaminants such as Sr are incorporated in the secondary calcite (Walton, *et al,* 1997, Curti,1998) while unreactive species may show increased diffusion as a consequence of microcrack development (Walton *et al,* 1997), or lower diffusion in high w/c cements (Sarott *et al,* 1992)

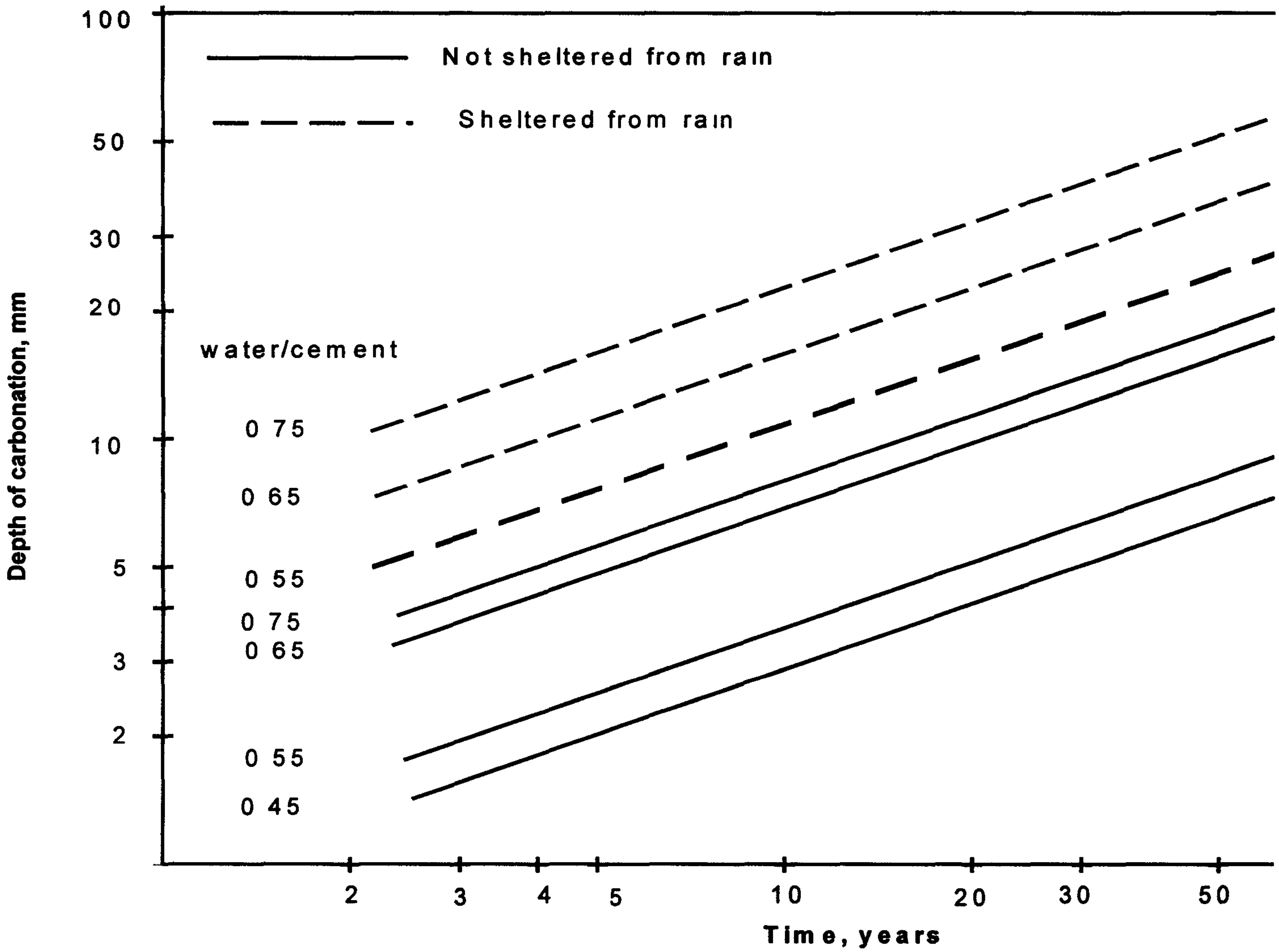

Figure 2 Measured mean carbonation depth in Portland cement concrete with varying water/cement ratios After Tuutti, (1982), Lagerblad & Tragardh, (1996)

5.4 Sulfate, Magnesium and Chloride attack

Accelerated degradation of hardened OPC concrete occurs by the formation of secondary sulfate phases, by reaction of hydrated cement phases with groundwater sulfate Formation of sulfate minerals results in a volume increase which eventually produce expansion, and may result in fracturing and spallation of concrete Ettringite is the sulfate phase most commonly associated with sulfate attack and forms by reaction of calcium aluminates and monosulphate (C_3A $CaSO_4$ $12H_2O$) in OPC Ettringite is a primary component of hydrated cement resulting from the inclusion of gypsum to control setting time Secondary ettringite forms by further reaction of sulfate in groundwater Sulfate-resisting cements are formulated which contain a low proportion of alumina to reduce ettringite formation in sulfate waters At increased sulfate concentrations gypsum ($CaSO_4$ H_2O) forms by reaction of $Ca(OH)_2$, in 5% sulfate solution ettringite and gypsum form concurrently (Ferraris et al 1997a) Expansion of cement exposed to sulfate solutions occurs initially by a diffusion controlled mechanism until available porespace is filled by gypsum and ettringite, cracking then follows which allows further access of sulfate solution to unreacted monosulphate (Pommersheim and Clifton, 1994)

In the presence of both sulfate and carbonate the mineral thaumasite ($CaSiO_3$ $CaCO_3$ $CaSO_4$ $15H_2O$) can form from alteration of CSH phases Since CSH is the main binding agent in the cement this form of sulfate attack results in complete breakdown to a dissaggregated mush (Crammond and Halliwell, 1997) Thaumasite attack is limited in occurrence and is favored by low temperatures and use of limestone and in particular dolomite aggregate

Magnesium sulfate solution is more deleterious to concrete than alkali sulfates because CSH phases are attacked as well as the aluminous phases Under the high pH conditions of the cement pore fluid brucite ($Mg(OH)_2$) precipitates and lowers pH, so that the CSH is destabilized, CSH then forms gypsum and free silica as follows

$$3CaO\ 2SiO_2 + MgSO_4\ 7H_2O = CaSO_4\ 2H_2O + 3\ Mg(OH)_2 + 2\ SiO_2$$

There is a net expansion during this reaction that results in fracturing, the formation of brucite produces a hard skin on the surface of mortar and concrete and this can restrict further attack

The extent to which sulfate attack will take place will depend on the sulfate concentration of percolating groundwater Secondary ettringite will only form if the groundwater has a higher sulfate concentration than that of the cement equilibrated pore solution The sulfate concentration of the cement porewater is controlled by temperature and alkali content (Lagerblad & Tragardh, 1996) and can vary between 0 1 and 100 mM/l SO_4^{-2} (Damidot *et al* 1992) No precise groundwater SO_4^{-2} concentration can be specified at which sulfate attack becomes significant A significant loss of compressive strength occurs after one years storage in 5% sulfate (Lea , 1980), while at a concentration of 0 5% sulfate magnesium sulfate attack is significant but sodium sulfate has little effect Atkinson and Hearne (1990) have developed a mechanistic model to predict the long-term durability of concrete exposed to sulfate groundwater

Chloride ions in groundwater can have a similar effect on concrete degradation as sulfate Normal cements have very low chloride contents to avoid corrosion of steel reinforcement Chloride ions bind to the AFm phase and produce Friedel's salt $3CaO\ Al_2O_3\ CaCl_2\ 10H_2O$, at very high concentrations of chloride the phase trichloride $3CaO\ Al_2O_3\ 3CaCl_2\ 32H_2O$ is formed The action of chloride may also produce reactions in the sulfate cement phases (Lagerblad & Tragardh, 1996) where chloride replaces sulfate in monosulphate that then is available to produce ettringite Reactions among chloride and sulfate cement phases are dependent both on temperature and chloride content The AFm chloride phase is stable between 10 and 1000 mmol/l Cl at 25°C (Atkins *et al,* 1994) Chloride concentrations of around 300 mmol/l and temperatures above 50°C are required to produce decomposition of ettringite (Lagerblad & Tragardh, 1996)

5.5 Alkali - aggregate reactions

Quartz and other rock forming minerals are unstable under the strongly alkaline conditions produced by the presence of sodium and potassium hydroxide in concrete pore solutions Crystalline minerals such as quartz are however slow to react even under strongly alkaline conditions More reactive forms of silica such as opal, chalcedony and glassy acid to intermediate volcanic rocks are liable to react to form an alkali-silica gel and CSH Formation of these phases as alteration rims around aggregates produces expansive forces, which may result in cracking (Ferraris *et al*, 1997b) and exhudation of a soft viscous gel (Lea, 1980) Such alkali-aggregate reactions are dependent on the alkali content ($Na_2O + K_2O$), below 0 6% Na_2O usually no deleterious alkali-silica reactions occur over short time-scales (100 years) (Lagerblad & Tragardh, 1996) Formation of alkali -silica gels removes alkali and lowers pH and this induces dissolution of $Ca(OH)_2$, released Ca may then exchange with alkali-silica gel to release alkalis and induce further alkali-silica reaction (Wang and Gillot 1991, Lagerblad & Tragardh, 1996) The rate of alkali-aggregate reactions is controlled by the rate of diffusion of alkalis to the reaction site within the aggregate or on the aggregate surface and by the dissolution rate of silicates Silicate dissolution rates are strongly pH dependent and increased at high pH (Lasaga, 1984) Contact of groundwater with concrete will clearly reduce the susceptibility for alkali-aggregate reactions by removing alkalis and lowering pH

5.6 Corrosion of steel reinforcements

Corrosion of steel reinforcement (rebars) results in expansion and ultimate fracturing of concrete Formation of FeO from Fe results in doubling of volume, while the formation of ferric hydroxide ($Fe(OH)_3 \cdot 3H_2O$) increases volume by a factor of 6 5 (Li and Li, 1997) Steel corrosion is thought to be limited under the high pH conditions due to the formation of a passivating protective surface (Wheat *et al*, 1997) Corrosion is induced in concrete by the effects of chloride and carbonation Chloride-induced corrosion is generally considered more important (Li and Li , 1997, Constantinou and Scrivener, 1997), largely because the effects of carbonation are slow

A number of mechanisms are likely to be responsible for chloride-induced corrosion (summarized in Wheat *et al*, 1997), chloride may attack the protective film/substrate bond without attacking the passivating layer or the layer may be chemically attacked Other theories propose that chloride is preferentially adsorbed in competition with dissolved oxygen and hydroxyl ions, or that chloride ions may penetrate the oxide film more easily than other ions Once the passivating layer is broken galvanic corrosion occurs Steel corrosion rapidly consumes dissolved oxygen and then produces hydrogen and establishes reducing conditions

Carbonation-induced corrosion proceeds by lowering the pH of the concrete pore fluid below that at which a passivating layer forms Although the rate of carbonation is affected by the quality of the concrete (water/cement ratio), once corrosion is initiated the initial properties of the concrete have no effect (Constantinou and Scrivener, 1997)

5.7 Biodeterioration of Concrete

Biodeterioration can be defined as any undesirable changes in the properties of a material by the activity of organisms i e plants, animals and microorganisms In the specific case of concrete the organisms of interest are on the whole microorganisms, and these organisms will be the focus of this section Microorganisms are ubiquitous in all natural and man made environments and have been associated with the deterioration of many commercially important materials including construction materials such as steel, stone and concrete This chapter will describe the processes by which microbial biodeterioration of radioactively contaminated concrete can take place, present examples from other industries where appropriate and outline the factors which influence the rate and extent of biodeterioration

5.7.1 Microbially Induced Degradation of Concrete and Cement

Microbially induced degradation of cement based materials or MID has been extensively studied in the nuclear industry due to its potential role in the deterioration of containment in cemented waste forms (Rogers et al 1993a,b, 1994, 1996) and has even been developed into a biologically based decontamination process for surface contaminated concrete (Rogers et al, 1997) In non-nuclear industries MID has been associated with the degradation of sewage pipes, water distribution systems, power station cooling towers and buildings (Rogers 1993a)

MID has two main aspects, firstly the deterioration of the concrete surface by the action of microorganisms resulting in a loss of structural integrity This results in the surface of the concrete being susceptible to sloughing off carrying any associated radionuclides with it Secondly microorganisms have the ability to secrete complexing agent which may mobilize radionuclides which are weakly bound to the concrete Once complexed in this manner these radionuclides are susceptible to further mobilization via water flow for example

Direct deterioration of the concrete surface occurs when microorganisms growing on the surface of the concrete generate acidic compounds which attack the concrete in the same manner as chemical acid attack The fact that in MID the process is microbially mediated usually results in the impact being more severe than direct chemical attack This is because the microorganisms grow in intimate contact with the surface and consequently any acid generated impacts on the surface as a concentrated point source There are three well known types of microbially mediated acid attack which are outlined in figure 3 The primary mode of acid attack is one of enhanced leaching where the inherent alkalinity of cement pore fluid is neutralized and alkalis and calcium are removed as soluble salts The specific soluble salts formed depends on the specific acid involved in the attack

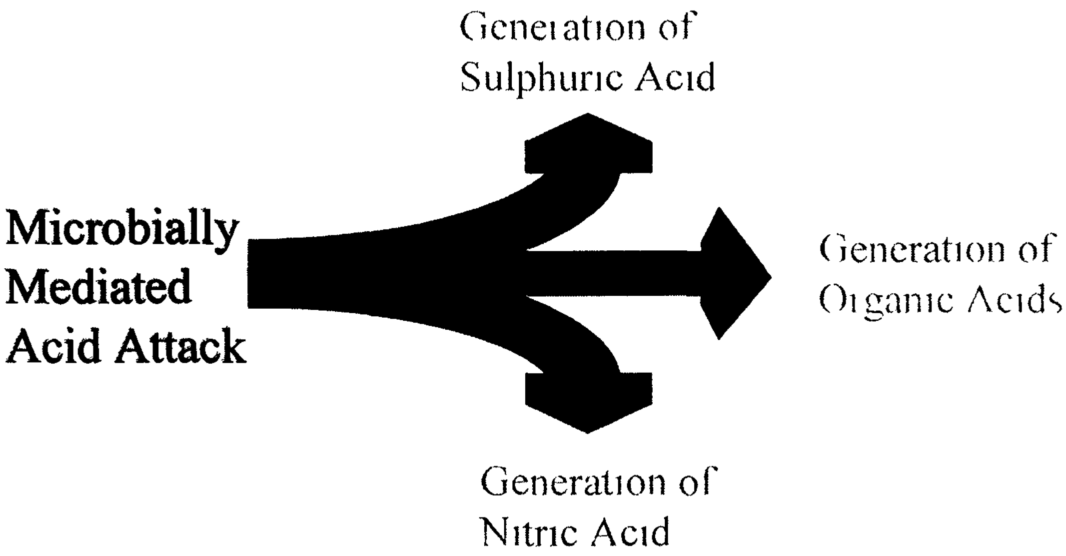

Figure 3 Types of Microbially Mediated Acid Attack

The generation of sulfuric acid is catalyzed by sulphur oxidizing bacteria with bacteria from the genus *Thiobacilli* being most commonly associated with concrete degradation *Thiobacilli* species get their energy for growth from the oxidation of reduced sulphur compounds with the subsequent generation of sulfuric acid The majority of these bacteria use molecular oxygen to drive this oxidation but there are species which can use nitrate in the absence of oxygen This group of bacteria has a wide tolerance to acidity with *Thiobacilli* species growing at pH's ranging from pH 6 5 to below pH 4 0 (Smith and Strohl 1991) The bacteria deposit sulfuric acid directly on the surface of the concrete as they grow Since sulfuric acid will react with and destroys Portland cement at any temperature above freezing (Hall 1989) this form of MID can have a devastating effect on any concrete structure under attack The result of sulfuric acid attack is a loss of granular structure and the formation of sulfate salts such as gypsum (Rogers et al 1993a) Sulfate may also be available for attack of AFm phases forming ettringite

In order for *Thiobacilli* species to grow they require sources of oxygen, carbon dioxide and reduced sulphur In nature the reduced sulphur source is generally found in the form of pyrite Pyrite oxidation is commonly associated with a specific species of *Thiobacilli*, *Thiobacillus ferrooxidans* This bacteria can oxidize both reduced iron and sulfide to generate energy for growth, and is the key species in the generation of acid mine drainage and microbial mining of metals such as copper and nickel (Brierley and Brierley 1997) In other cases *Thiobacilli* species may grow on reduced sulphur compounds generated by another group of bacteria, the sulfate reducing bacteria (SRB) This is important since it allows sulfuric acid based MID to occur where no obvious source of reduced sulphur exists In this situation the sulfate reducing bacteria reduce sulfate to generate hydrogen sulfide as part of normal growth This process occurs under strong reducing conditions, the sulfide generated then migrates into an oxidizing environment where *Thiobacilli* species are able to utilize it generating sulfuric acid as a by-product The classic example of this cycling of sulphur resulting in concrete degradation is in sewer systems Here SRB's are able to grow in the liquid waste in the bottom of the sewer pipes generating hydrogen sulfide This migrates as a gas into the body of the sewer pipe with some of it dissolving into condensation on the concrete surface Here, where there is both a source of oxygen and sulfide *Thiobacilli* are able to generate sulfuric acid This mechanism has been responsible for catastrophic failure of the sewer system in Hamburg, Germany (Rogers et al 1993a)

Nitric acid attack is similar to sulfuric acid attack in that a bacteria catalyses the generation of acid through the oxidation of a reduced compound during its growth This is classically caused by two groups of bacteria collectively known as nitrifyers The first group oxidizes ammonia to nitrite and the second nitrite to nitrate Both reactions liberate hydrogen ions and generate nitrous and nitric acids respectively The bacteria responsible for these reactions are common in soils and aquatic environments such as river beds Unlike the sulphur oxidizing bacteria, the nitrifyers and specifically those responsible for ammonia oxidation, are sensitive to low pH's This means that nitrogen base MID is self regulating and does not generate the low pH's associated with the growth of *Thiobacilli* species

Nitrifyers have been isolated from corroded concrete and implicated in the corrosion of stone with acid depleting the binding material (Rogers et al 1993a) A classic example of nitric acid MID has occurred on Cologne cathedral and other sandstone buildings in Germany (Rogers et al 1993a)

The bacteria responsible for the generation of organic acids are a much more diverse group than those discussed up to now in this section These heterotrophic bacteria generate energy for growth through the consumption of complex organic compounds and may generate a wide variety of organic acids as by-products of their growth These acids include acetic, lactic, citric, gluconic etc , all of which may attack cement based materials The wide variety of organisms that fall into this category means that they are very widely distributed in all environments, particularly soil The role of heterotrophic bacteria in MID is not as extensively studied as that of the sulphur oxidizers or the nitrifying bacteria However, they have been isolated from concrete corrosion sites and it is suggested that they play a role in reducing the pH to a values which is more favorable for the growth of *Thiobacilli* species (Rogers 1993a)

5.7.2 Generation of Complexing Agents

From the point of view of radioactively contaminated concrete, organic acid attack has an additional effect that may be important This is the fact that these acids and particularly citric acid, can complex radionuclides resulting in an increased solubility In the case of citrate plant roots and fungal hyphae have been implicated in its release into soils (White et al 1997) The degree to which complexation is a factor will depend on the manner in which the radionuclides are immobilized on the concrete surface It is possible that the action of direct acid attack and complexation act in concert With the acid attack resulting in the radionuclides becoming more susceptible to complexation since their attachment to the concrete is weaker

In addition to the organic acids microorganisms are known to produce a whole range of organic molecules that can complex metals These include siderophores that are specifically excreted under iron limiting conditions, and metal binding proteins such as metallothioneins The extent to which these compounds are important in the mobilization of radionuclides is difficult to assess and their generation may be a source of significant uncertainty However, 2-ketogluconic acid has been implicated during the weathering of silicates (Webley et al 1963) and oxalates during basalt weathering (Silverman and Munoz 1970) Complexation by these compounds cannot therefore be neglected in consideration of risks

5.7.3 Factors Influencing Biodeterioration

In order to assess the impact of biodeterioration on concrete and the release of radionuclides it is important to understand the factors that control biodeterioration Although the surfaces on which microorganisms are growing during MID are generally inert the organisms must be in contact with an environment which provides them with the nutrients they require to grow The major controlling factors for biodeterioration are outlined below

5.7.4 *Water availability*

Water is essential for microbial growth, consequently without an adequate amount of water MID will not proceed This water may be provided as a liquid or a vapor and could come from the surrounding soil for a buried structure or from humidity for a above ground structure The influence of water on the extent of MID is such that it may proceed intermittently in environments where there are pronounced wet and dry seasons

Water logging can also have a marked effect on the activity and types of microorganisms present in soil This is because under these conditions oxygen generally becomes limited and anaerobic conditions prevail This would promote the generation of organic acids such as acetic acid but retard *Thiobacilli* species and nitrifyers

5.7.5 *pH*

The pH can have a significant effect on the growth of microorganisms with each species having a specific range and optimum under which it grows As we have already discussed the pH range for *Thiobacilli* species and therefore sulfuric acid attack is very wide, where as that for nitrifyers and nitric acid attack is narrower In the case of concrete degradation the surface pH may have to be lowered through carbonation for example, before *Thiobacilli* species can take hold This lowering of the initial pH may also be achieved by the presence of heterotrophic microorganisms generating organic acids

5.7.6 Nutrients

The availability of nutrients is key to the progress of MID If there are no reduced sulphur sources or reduced nitrogen source available then MID via *Thiobacilli* species or nitrifyers will not proceed On the other hand if there is insufficient oxygen, then the availability of these sulphur or nitrogen compounds will not be important since the system will be oxygen limited In terms of heterotrophic generation of organic acids the key will be the availability of organic substrates in the soil to drive the generation of the acids The most important variable in assessing the likelihood of the various types of MID is therefore the availability and quantity of the particular nutrients required to drive the process

The situation with the complexing agents may be more complex This is because some of these compound are generated by microorganisms in response to nutrient shortages and in effect represent a survival strategy

5.7.7 Temperature

As with pH microorganisms have a optimum and a range of temperatures over which they grow Under environmental conditions the general trend is as the temperature increases so does microbial activity As with water availability this may have the effect of producing seasonal variations in the extent and rate of MID

5.7.8 *Presence of Microorganisms*

Generally the presence of the particular microbes associated with MID is not a controlling factor This is because all the organisms involved are ubiquitous in all natural and man made environments In many cases they have the ability to stay dormant for long periods of time until the conditions which are favorable for their growth become available

5.8 Colloid Generation in Cementitious Systems

Very fine-grained suspended solid material can potentially act as a separate transport mechanism for radionuclides to that of dissolved species transport Plutonium and other actinides may form aggregates of polymeric aqueous species (true colloids) and these are discussed in the section on speciation Radionuclides may also be transported as sorbed material onto inorganic(mineral) and organic particulates (pseudocolloids) Such material is typically in the size range 1nm - 1µm (Kim *et al*, 1997) A number of studies of natural groundwaters including analogues of actinide contamination have shown that a significant proportion of radioactivity can be present in groundwater present on such pseudocolloids (Olofsson *et al*, 1986, Kim *et al*, 1987, 1989,1997,Longworth *et al*, 1989, Miekeley *et al*, 1989, Dearlove *et al*, 1989) Colloidal material which has been shown to sorb actinides includes, organics (humics), iron hydroxides, clay minerals, silica, and other silicate minerals (feldspar)

Direct investigation and characterization of colloid formation in cementitious systems has been made by Ramsey *et al*, (1988)(see also Gardiner *et al,* 1997) Colloids formed in leachates from OPC were filtered to collect various size fractions and were examined by electron microscopy, X-ray diffraction and bulk chemical analysis (ICP-AES, ICP-MS) Colloids collected were composed of CSH and effectively represent fine - grained cement matrix Colloids produced showed significant sorption of radionuclides including uranium Leaching of OPC in these experiments was performed in closed flasks purged with nitrogen, thus eliminating carbonation, it would be expected that fine-grained suspended CSH material would undergo carbonation in an open system with freely available CO_2 During carbonation CSH produces amorphous silica which may form colloidal material

In order to increase radionuclide mobility significantly sufficient colloid particles must be present in suspension Gardiner *et al,* 1997 have considered the processes controlling colloid particle growth and aggregation, nucleation, temperature and ionic strength are factors which govern the colloid concentration in experiments on colloid generation from OPC leachates Gardiner *et al* comment that when included in the Nirex 97 risk assessment of the post-closure radiological safety case of a U K repository cement generated colloids did not significantly increase risk Bradbury and Sarott (1994) also comment on the ability of cementitious colloids to significantly increase the total concentration of radionuclides in the aqueous phase of the near-field repository environment, since CSH is the major component of both colloids and cement solid phase sorption properties will be similar Bradbury and Sarott (1994) conclude that unrealistic amounts of colloidal material (> 10 grams/litre) will be necessary to significantly increase aqueous phase radionuclide concentration Similar arguments may apply to the generation of colloids from carbonated concrete if it can be demonstrated that the solid substrate and colloid material are composed of similar materials

5.9 Ancient analogues of concrete degradation

Ancient analogues of modern OPC based concretes have been examined to provide information on the long-term behavior of concrete and mortar in radioactive waste repositories (Lagerblad & Tragardh, 1996) The greatest difficulty in applying such information is the variation in the composition and grain size of ancient cements Portland cement used in the early 20th century were coarser and contained a higher content of C_2S than that used today OPC based cements exposed to water for periods of the order of 100 years remain durable, there is evidence that cement phases requilibrate and form larger crystals, and in some cases there is evidence of reaction with cement aggregates Available examples show relatively little carbonation when immersed in water (5mm in 90 years, Lagerblad & Tragardh, 1996) More ancient Roman mortars and concrete over 2,000 years old which contained pozzolanic material resembling OPC type cements still show strong durability (Jiang and Roy, 1994) These cements are fully carbonated and contain only a small amount of calcium silicates (Majumdar et al, 1988) Carbonation occurs in these ancient buildings because of exposure to the atmosphere (Lagerblad & Tragardh, 1996) Modern pollution, in particular acid rain, has had a marked influence on the durability of some ancient monuments such as the Taj Mahal and the Pyramids (Roy and Jiang, 1997) and indicates the importance of modern sulfate and nitrates to concrete degradation

5.10 Repository degradation models

Long-term models have been devised to predict the structural and chemical evolution of concrete structures for low and intermediate level radioactive waste disposal Models have been proposed of varying detail, and considering various chemical and physical processes of cement and concrete degradation Lagerblad & Tragardh (1996) have produced a conceptual model for the chemical and structural evolution of a proposed Swedish deep nuclear waste facility This model identifies the processes and estimates the extent of chemical degradation during the periods of site development and post-closure, where differing groundwater, headspace gas composition and temperature conditions occur For this deep repository extremely long time-scales, of more than 100,000 years, are considered and only a qualitative description of the behavior of concrete is provided Mathematical models have been developed to quantitatively predict the service life of concrete buried near to the surface over periods up to 1000 years used to store low-level radioactive waste (Atkinson and Hearne, 1989, Reed et al, 1994 report, Snyder *et al*, 1996, Gerard *et al,* 1997, Lee *et al, 1*995) Most of these models utilize empirical analytical equations to model individual degradation processes such as sulfate attack, $Ca(OH)_2$ leaching, and carbonation Corrosion of steel rebar can be modelled by considering the diffusion of chloride to the steel and from an anoxic corrosion rate The model of Reed *et al* (1994) links these degradation processes to a structural analysis code that computes stresses in concrete and weakened rebar at various locations in a structural model Once stress in the rebar exceeds a certain threshold cracks develop in the concrete as a function of the structural design, at a higher threshold the rebars yield and additional stress is applied to other parts of the structure The model successively calls the concrete degradation and structural sub-models until some predefined state of collapse of the structure is reached Snyder *et al* (1996) consider the advective and diffusive transport of ions through a repository concrete slab and its associated degradation by sulfate attack, steel corrosion and $Ca(OH)_2$ leaching Gerard *et al* (1997) consider simultaneously the specific interactions between diffusion, leaching, mechanical strength, cracking and permeation Alcorn *et al* (1990) have derived a model to predict the hydraulic conductivity of OPC cement grout to be used as a cement backfill material, according to this model for an ambient hydraulic head of 1m/m the hydraulic conductivity remains below acceptable performance level (10^{-10} m/sec) for a minimum period of 30,000 years Adenot and Richet (1997) describe a model of purely diffusive reaction of water with cement paste which incorporates the chemical leaching behavior of CSH and the breakdown of monosulphate and ettringite According to Adenot and Richet (1997) for a good quality cement (water/cement = 0 4) a degradation layer composed of CSH and silica gel will extend a thickness of 1 2mm after 3 months and 4cm after 300 years Purely diffusive alteration of cement is limited by the build up of a protective layer of silica gel, if this gel is removed by some other process such as erosion or chemical dissolution then degradation is more severe

5.11 Concrete degradation relevant to radionuclide mobility at Rocky Flats

Concrete degradation effectively controls release of actinide contamination by allowing free access to moving groundwater Concrete has a low permeability compared to soil material and therefore it is unlikely that there will be significant water flow through concrete blocks buried with soil, flow will concentrate around the outside of concrete blocks The bulk of the contamination in RFETS concrete is present in the upper few millimeters of concrete The mobility of radionuclide contamination will therefore be primarily controlled by the zoned chemical degradation formed on the surface of the concrete The nature of the degradation will clearly depend on the groundwater environment and geochemistry

The background groundwaters at RFETS within the upper hydrostratigraphic unit are typical dilute Ca bicarbonate waters, whereas groundwater at depth in the lower unit are more sodium rich and more variable The upper hydrostraigraphic unit is variable in thickness from 10 ft to 130 ft therefore it is likely that buried concrete will be in contact with a dilute Ca bicarbonate water Such water is unlikely to produce enhanced degradation of AFm phases in the cement matrix by attack by sulfate, chloride or magnesium In the industrial area however, there are some high concentrations of sulfate over 1000mg/l, these concentrations are likely to produced enhanced degradation by formation of secondary ettringite Concrete buried in the unsaturated zone is likely to be subjected to carbonation CO_2 partial pressures in soil gases are typically above that of the atmosphere as a result of respiration by plants and microorganisms, and thus carbonation will probably be accelerated during burial Partial pressures of CO_2 calculated from speciation calculations are not summarized in the RFETS Site Characterization Report (EG&G, 1995) The example WATEQF output in Appendix H of the Groundwater Geochemistry Report however gives a CO_2 partial pressure of 6 93e-2 atm which is above the maximum of CO_2 levels normally measured in soils (log pCO_2 = -1 5 Appelo and Postma, 1994) While this value may not be typical CO_2 contents are likely to be significantly above that of the atmosphere, and will thus promote carbonation Fujiwara *et al* (1992) examined concretes buried in soil for 60 years in saline groundwater, they observed that calcite was the main alteration product in the upper 10cm of the concrete, and that chloride alteration occurred at greater depth as a consequence of the saline water The samples examined by Fujiwara *et al* were in saturated water where carbonation is generally thought to be less effective More ancient Romanic concretes and mortars are virtually completely carbonated on exposure to atmospheric CO_2 There seems little doubt that the main chemical alteration of the surface contaminated layers of concrete at RFETS will be by carbonation

As discussed previously, carbonation results in a significant decrease in pH from above 10 5 for buffering by CSH and $Ca(OH)_2$ to around 7-8 buffered by calcite (Figure 1), this has important implications for the solubility and sorption of Pu, U and Am In general carbonated, weakly alkaline cements do not perform as well as fresh high pH matrices in immobilizing nuclear waste (Glasser, 1997) Carbonation of the surface of concrete results in a decrease in void space and an increase in durability Carbonation may therefore physically entrap particulate oxide contaminants, this could possibly have occurred already by atmospheric carbonation, or may occur subsequent to burial

Controls on the redox state of groundwaters at RFETS are largely undefined (EG&G, 1995), few reliable Eh measurements are available Field measurements do record dissolved oxygen, but reduced iron minerals such as siderite and pyrite and carbonaceous materials are identified in cores from the upper hydrostratigraphic unit (EG&G, 1995), such observations are typical of the disequilibrium of redox reactions in natural groundwater (Stumm and Morgan, 1981) Corrosion of steel rebar exposed to groundwater in demolished concrete will act as a reducant to produce reduced groundwater conditions, the effectiveness of this reducant will depend on the groundwater flux, the rate of corrosion and the dissolved oxygen content of the inflowing groundwater It has been discussed how microbial activity can effectively catalyze redox reactions and hydrogen produced by anaerobic corrosion could be utilized by sulfate reducing bacteria, and could conceivably reduce available sulfate, particularly in the industrial area where 1000 mg/l sulfate is measured Given the large climatic variation at RFETS seasonal variations could conceivably result in cylic reduction and oxidation of sulfate which gives rise to the classic sulfuric acid mediated form of microbial induced degradation (Rogers *et al*, 1993a) Sulfide is however likely to precipitate as iron sulfide if associated with steel corrosion and may not be available for subsequent oxidation by *Thiobacilli* Since sulfides are present in the local alluvium and bedrock, and there is no recorded evidence of sulfide oxidation then it would appear that microbial influences on cement degradation and controlling redox state are limited at RFETS Unless some other form of reduced substrate such as organic matter is disposed with buried concrete then it is likely that the prevailing background Eh will continue to apply

Modelling studies of the behavior of large concrete structures used in near-surface low-level radioactive waste disposal repositories indicate that their gross structure will survive intact for periods of around 1000 years (Reed *et al*, 1994, Gerard *et al*, 1997) After this time severe cracks will have developed allowing groundwater access to radioactive waste Buried concrete rubble at RFETS will not be subject to the same stresses as large intact structures, which promote the cracking and breakdown of large structures Degradation of buried concrete will be predominantly by microscopic-scale chemical and physical processes which will eventually lead to spallation of surface layers, where particulate and liquid contamination is concentrated The diffusion controlled cement degradation modelling of Adenot and Richet (1997) is more applicable to the degradation of buried concrete rubble since this describes the chemical degradation of the concrete surface exposed to a reactive fluid Considering that groundwater flow will be around concrete blocks rather than through the cement microporosity, diffusion will likely control the cement degradation reactions Adenot and Richet (1997) predict that for pure water diffusive degradation will extend 4cm after 300 years in good quality concrete Carbonation, which is expected to be the dominant degradation processes for buried concrete at RFETS, is likely to produce more aggressive alteration, although carbonation will tend to reduce permeability in the concrete surface and hence reduce diffusion Considering these modelling studies and evidence from ancient cements it is likely that chemical degradation will extend a distance of the order of 10cm during the 1000 year risk assessment period, which will include the majority of the surface contamination Uranium present in the aggregate is unlikely to be exposed to free-flowing groundwater during the 1000 year risk assessment period

Spallation of the surface layer will increase the accessibility of groundwater to radionuclide contamination Spallation is dependant on the nature of the degradation mechanism, carbonation improves durability and reduces the susceptibility to freeze-thaw mechanisms Sulfate attack and accelerated leaching by microbial activity breaks down the cement matrix allowing dissagregation of the surface layer

Possible colloidal materials generated from cement degradation are silica resulting from leaching and carbonation of CSH and iron hydroxides produced from steel corrosion Natural colloids may exist in the background groundwater in forms such as humics or suspended clay particles derived from weathering and erosion of bedrock claystones The additional effects of colloids generated from cement degradation should be assessed with reference to these background colloids, and to competition for sorption of radionuclides between colloids and the concrete matrix (Bradbury and Sarrott,1994)

6. Leaching of Actinides in Cementitious Systems

Direct experimental measurement of the leaching and diffusion of actinides in cementitious systems is much more limited than that of more mobile radionuclides such as cesium The Swedish Nuclear Fuel and Waste Management Company (SKB) have undertaken research, from 1980 to 1990, and the results have been summarized by Albinsson et al (Albinsson et al, 1993) The experiments described in this work involved the measurement of cesium, americium and plutonium diffusion into five different types of concrete The experiments were carried out over long time scales, 2 5 years for americium and 5 years for the plutonium

The experimental technique involved taking pre-aged concrete samples, with approximate length of 25 mm The samples were then dipped into radionuclide-spiked porewater, inside a glove-box to avoid significant uptake of carbonate At the end of the experiments, the concrete samples were ground, removing a 0 1 - 0 7 mm layer with each grinding Estimation of apparent diffusivity (D_a) was achieved either through activity measurements or, more accurately, through autoradiograms

The result was that no movement of plutonium or americium could be measured (0 2mm), despite the long time scales The D_a for americium from activity measurements was estimated at $1 - 9 \times 10^{-16}$ m^2/s, while autoradiogram measurements indicated a D_a of $<0\ 3 - 1\ 8 \times 10^{-17}$ m^2/s, with the variation mainly depending on how deep the grinding was, rather than the type of concrete used The Plutonium D_a was similarly low, with a range of values given by $0\ 8 - 2\ 4 \times 10^{-17}$ m^2/s, from activity measurements No autoradiograms could be taken, as almost all the activity was removed after the first grinding

The explanation for the low diffusion of these actinide elements is their high sorption onto concretes The R_d for americium sorption onto concrete varies between 1 and 10 m^3/kg, while the plutonium sorption is slightly lower (R_d = 1 to 5 m^3/kg) The higher sorption exhibited by americium would suggest that its D_a should be lower than plutonium, when in fact the reverse is true This may suggest that the sorption - only mechanism is not the whole story However, the fact that sorption is so high, and that the differences between the two actinides is small, means that the evidence is not clear cut

European Community sponsored research has also focused on the leaching behavior of radionuclides from cemented waste (Vejmelka et al, 1991) This series of experiments first looked at the behavior of uranium, plutonium, americium and neptunium in cement samples, in a Q-brine ($MgCl_2$ rich solution) and NaCl brine

To accelerate the leaching process, crushed samples were used The pH of the Q-brine/cement solution was found to be 6 5, while the NaCl-brine/cement solution was at pH 12 5 Plutonium loadings were varied between 10^{-9} and 10^{-5}g/g cement, neptunium between 10^{-6} and 10^{-4} g/g cement, and uranium from 10^{-4} to 10^{-1}g/g cement These amounts roughly correspond to the levels found in real waste encapsulation

The results showed, for the Q-brine solution, a linear increase in americium and neptunium aqueous concentrations with increasing actinide loading This indicates that sorption is the dominant factor in the determination of aqueous concentration The results for plutonium are not shown, but the text mentions that the same behavior is observed for plutonium Uranium exhibits similar behavior below loadings of 0 01 g/g cement, above this concentration, a constant aqueous concentration of 5×10^{-5}M is observed, which corresponds to the solubility limit of $UO_2(OH)_2$ This was confirmed by the presence of a yellow precipitate

In NaCl solutions, the high pH means that solubility controls the aqueous concentrations of all of the actinides The main conclusion from this portion of the work is that the concentration for Am, Np and Pu is limited to 1e-8M to 1e-10 M (for both brines) and 1e-5M for uranium

An important conclusion is that the behavior of the actinides is independent of the doping technique Thus the same result is observed whether the actinide was incorporated into the cement or added later into the solution

It was also discovered that the aqueous concentration of Am was not effected by the presence of cerium, indicating that cerium does not compete with americium for sorption sites, and that ion exchange is not a likely mechanism for radionuclide sorption onto cement materials

The kinetics of leaching from cement encapsulated materials was also examined For Americium, the composition of the brine had no effect on the leaching behavior, while for plutonium, the low solubility of plutonium hydroxides meant that the experimental concentrations were below detection limits in the NaCl brine The results showed that the effective diffusion coefficient for Pu was 1×10^{-16} m^2/s, and for americium the value was 2×10^{-17} m^2/s

The leachability of Nd (an analogue of trivalent actinides), uranium, thorium and strontium have been examined in a CO_2 free environment (Serne et al, 1996) Crushed cement samples containing these four radioelements were placed in deionized water, and the aqueous concentrations measured at a range of pHs, and at different times The results showed that equilibrium was reached, in all cases, within 2 days Neodymium aqueous concentrations fell steadily with increasing pH (from 7 to 9), and were at the analytical detection limits at pHs above 9 The solubility limits of $Nd(OH)_3$ were shown to approximate the observed results well Similar results were observed for uranium, and the aqueous concentrations could be explained by the equilibrium with $CaUO_4$ Thorium aqueous concentrations were at or below the detection limit over the whole pH range, this is probably due to the formation of the insoluble $ThO_2(am)$ phase Strontium leached concentration indicated no pH variation, but the prospect of precipitating strontium carbonates in a real groundwater system cannot be ruled out

The conclusion from this work is that solubility, rather than adsorption is the dominant factor in determining leaching of actinides from cementitious materials, provided the contaminants are present at > 0 15% of the cement waste form

6.1 Conclusions on Leaching Experiments

It is difficult to make any firm conclusions based on the limited amount of data presented here However, the following observations can be made

1 The penetration of actinide elements into a cement waste form is limited, even when the radionuclides are initially in the aqueous phase This supports the assumption that the contamination of concretes at RFETS will be surficial in nature, and concentrated within the first few millimeters of the concrete
2 The factors controlling actinide leaching from concrete are solubility and sorption The predominance of one over the other will depend on the concentration of each actinide originally present in the concrete
3 The fact that the contamination at RFETS will be surficial, rather than analogous to encapsulated waste, and leaching determined by sorption and solubility means that sorption and solubility data from the literature can be used to estimate leaching Diffusion processes are not relevant to this study

7. Behavior of actinides in cementitious environments

The lack of much real actinide leaching data means that the chemical behavior of the elements in a cementitious environment must be investigated to aid elucidation of likely leaching behavior at RFETS The limited site data suggests that the contamination is likely to be particulate, particularly PuO_2 Thus, the first factor in determining the leach rate from the surface of the concrete is the solubility of these minerals Once in the aqueous phase, the actinides will come into contact with the cement matrix itself, with the possibility of sorption further retarding the movement into the groundwater

Therefore, this section examines the available literature data concerned with actinide sorption and solubility in cementitious environments A fully comprehensive review of the environmental behavior of actinides is not reported here Rather, the essential features of actinide solubility and sorption behavior have been explored From this, it is hoped, a preliminary picture of the factors influencing actinide leaching from concrete surfaces will begin to emerge

7.1 Summary of Conditions expected in a cementitious environment

The evolution of the chemistry in cement porewaters has been described earlier (Figure 1) and it has been concluded that carbonation will have a significant effect on the behavior of concretes close to the surface This impacts on radionuclide behavior in two ways Firstly, formation of calcite drops the pH of the porewater solution significantly to ~8, which could impact on radionuclide solubility and sorption Secondly, the formation of calcite presents a different surface to the actinides, and a consequent change in sorption behavior Also, actinides form strong carbonate species in aqueous solution, and this can reduce sorption and increase solubility

The redox conditions in the immediate environment of the contaminated concrete will also be an important factor in the determination of actinide leaching behavior The redox potential within the cement porewaters will depend on the composition of the cement Ordinary Portland cements are poorly poised, and so the redox potential is easily influenced by the groundwater in contact with it Cement blends containing significant amounts of blast furnace slag will produce reducing porewaters, due to the presence of iron sulfides, which creates a SO_4^{2-} /HS^- poised system (as well as other sulphur couples) The result is a measured Eh of ~200 mV (Glasser, 1991) However it is unlikely that the concretes at RFETS will contain significant quantities of slag

Corrosion of the steel reinforcements is another source of potentially low Eh values As these rebars corrode, the Eh is lowered to hydrogen liberation potential This mechanism may lower the Eh of the bulk concrete porewater, however, the majority of the actinide contamination is on the surface of the concrete structures Therefore, it is more likely that the redox conditions of the concrete surface will mirror very closely the redox of the groundwater According to the geochemical characterization (EG+G, 1995), the redox potential indicates slightly oxidizing conditions (90 - 320 mV) Microbial activity could potentially lower this Eh on the concrete surface, but evidence for this is lacking at present

In summary, the actinides present on the surface of concrete at RFETS would, on burial, experience alkaline conditions, due to concrete degradation However, the influence of the groundwater is likely to be large, with carbonation of the concrete surface a very likely outcome The result would be a lower pH of ~8 Redox conditions are likely to be mildly oxidizing, due to the lack of redox poising from the concrete, and the consequent influence of the groundwater

7.2 Speciation of Actinides

7.2.1 General

The actinide series of elements results from the filling of the 5f orbitals, the series beginning with thorium and ending with lawrencium The ionization energies of the 5f electrons plays an important role in the chemical behavior of the actinide elements The ionization energies of the actinide elements are significantly lower than those of analogous lanthanide elements, the reason being that the 5f orbitals are considerably more shielded from the nuclear charge than the 4f electrons Thus, the 5f electrons are less firmly held than the 4f electrons in the lanthanide elements, and so more available for bonding

The electronic structure has important implications for the available oxidation states for the actinide elements The similar energies of the 7s, 6d and 5f electrons means that multiple oxidation states are accessible, particularly for the first half of the series In contrast, the lanthanides are almost exclusively found in the 3+ oxidation state Table 1 (Katz et al,1986) lists the oxidation states that uranium, plutonium and americium can form, with the most stable oxidation state indicated in bold

Element	Ground state electronic structure	Oxidation states
Uranium	[Rn] $5f^3 6d^1 7s^2$	3,4,5,**6**
Plutonium	[Rn] $5f^6 7s^2$	3,**4**,5,6, (7)
Americium	[Rn] $5f^7 7s^2$	**3**, 4, 5, 6

Table 1 Oxidation States of U, Pu and Am

The oxidation state of each actinide is crucial in the determination of its mobility In general, the reduced oxidation states are less mobile, exhibiting greater sorption and lower solubility (Choppin et al, 1995) Each element will also behave differently in terms of aqueous speciation, depending on the oxidation state

Actinides in the same oxidation state have the same structure Actinide ions in the 3 and 4 oxidation states are in form of simple hydrated An^{3+} and An^{4+}, although these simple ionic forms have a strong tendency for hydrolysis and polymerization unless in acidic solutions (Katz et al, 1986) Actinides in the higher oxidation states form oxygenated, actinyl species in solution, AnO_2^+ and AnO_2^{2+} These structures are very stable in aqueous solution, possess a linear structure (Greenwood and Earnshaw, 1984) and reduce the effective charge on the central actinide ion, for example, the charge on the Pu atom has been reported as +3 2 and +2 2 for the PuO_2^{2+} and PuO_2^+ ions respectively (Silva and Nitsche, 1995)

Hydrolysis is an important reaction in natural waters, and has a large influence on actinide behavior In general, hydrolysis decreases in the order,

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$$

which is expected from charge to ion size ratios Hydrolysis is important in that it can alter dominant oxidation states For example, the greater hydrolysis of An(IV) species relative to An(III) results in greater stability for the An(IV) ion Hydrolysis is also important in terms of the formation of polymers, (Pu colloids) with Pu(IV) being particularly susceptible (Toth et al, 1983, Choppin et al, 1995) Plutonium polymers are very stable and not easily depolymerized, and, as the effect of, for example, concentration, temperature and ionic strength is not well understood, the erratic nature of Pu(IV) aqueous solutions can make predictions of behavior difficult (Katz et al ,1986)

The mobility of actinides in the environment is determined, to a large extent, by its solubility and sorption, and the results of specific experiments are presented in the following sections The extent of both precipitation and sorption is influenced by aqueous complexation, which can reduce the extent of both processes For example, the sorption of metals onto iron oxides is reduced in CO_2 environment, at high pH, relative to sorption in a CO_2-free atmosphere (Waite et al, 1994) In general, the trend of strengths of complexation of various ligands with actinide ions is given by,

$$OH^-, CO_3^{2-} > F^-, SO_4^{2-}, HPO_4^{2-} > Cl^-, NO_3^-$$

Thus, the main ligands that could perturb the sorption or solubility of actinides at RFETS will be carbonate, which is the dominant ion in RFETS groundwaters, and sulfate which is present in elevated concentrations at various locations (EG+G, 1995) Complexation of actinides by organic ligands is also well known (Katz et al, 1986) at RFETS organic ligands could be produced by microbial activity as described earlier, or by organic contaminants

7.2.2 Plutonium

Plutonium forms a number of oxidation states that are stable in natural waters Pu(III) is stable under acidic conditions, although it is easily oxidized to Pu(IV) PuO_2^+ disproportionates to Pu^{4+} and PuO_2^{2+}, although there is some evidence that it may be the dominant species in solution when concentrations are low, and the chances of two PuO_2^{+} ions interacting is very small (Choppin, 1983) PuO_2^{2+} is stable but can be easily reduced, even by the action of its own α radiation (Katz et al, 1986) The dominant control of plutonium in natural waters is provided by the stability of the PuO_2 phase (Stenhouse, 1995), with the degree of crystallinity being the dominant factor in controlling plutonium concentrations The environmental behavior of plutonium can be described schematically, as in Figure 4 (Choppin et al, 1995)

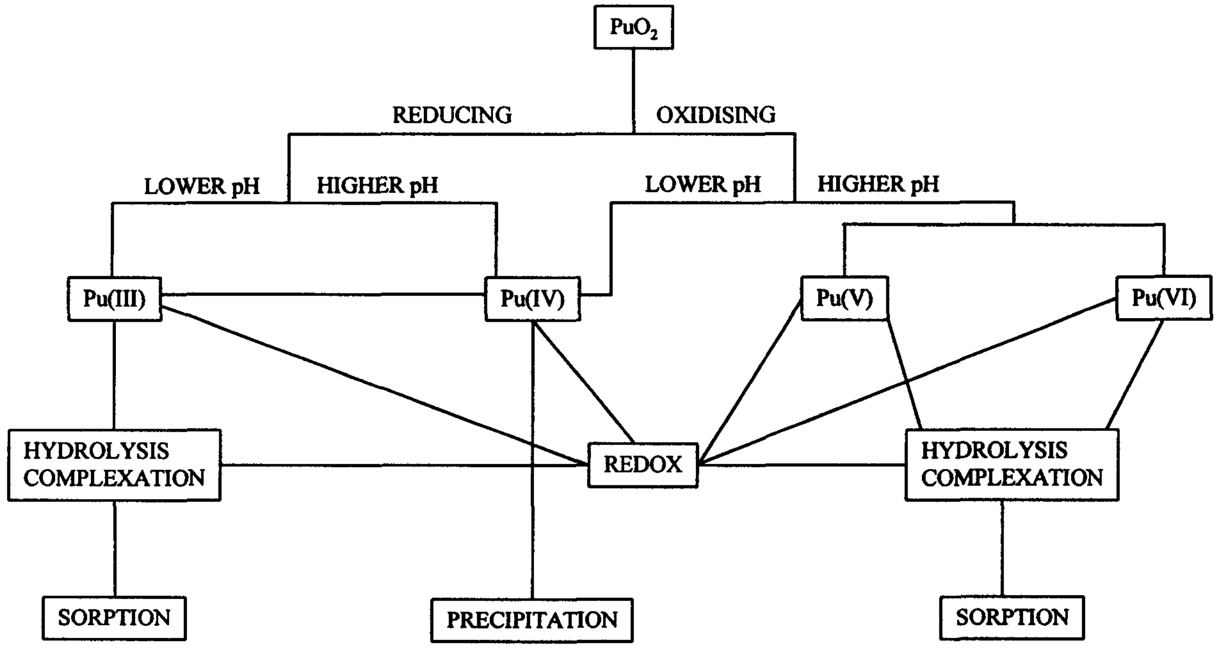

Figure 4. Schematic Representation of the environmental reactions of plutonium

7.2.3 Uranium

Uranium can form three stable oxidation states in natural waters, U^{4+}, UO_2^{+} and UO_2^{2+} UO_2^{2+} is the most stable form of uranium in aqueous solution, and is difficult to reduce (Katz et al, 1986) UO_2^{+} disproportionates to U^{4+} and UO_2^{2+}, while U^{4+} is stable with respect to water but is slowly oxidized by air to UO_2^{2+} Rai et al (1990) note that oxygen fugacities must be below 10^{-65} in order to maintain uranium in the U(IV) oxidation state

The uranyl ion is the most stable actinyl ion, with a U-O bond distance of 180pm (Greenwood and Earnshaw, 1984) Uranyl forms a large number of aqueous species, of which uranyl carbonates dominate at neutral pH in natural waters Below pH 5, the uranyl ion and UO_2OH^{+} dominate aqueous speciation The U^{4+}, like all An^{4+} ions, is easily hydrolyzed above a pH of around 2 9 (Katz et al 1986), and its speciation is dominated by UOH^{3+} at low pH, and $U(OH)_4^{0}$, and possibly $U(OH)_5^{-}$ (although the presence of this species has been disputed (Rai et al, 1990) at higher pH's

Solubility control is sometimes difficult to assess due to the complex solid phase chemistry of uranium, with over 160 uranium containing minerals identified (Smith, 1983) Most of the uranium found in natural deposits is in the form of uraninite (UO_{2+x} (0 0<x<0 25)), indeed it was previously thought that all uranium was originally deposited as this mineral, with oxidation resulting in the formation of other minerals Dissolution of uraninite under oxidizing conditions can produce a whole wealth of secondary mineral phases, depending on groundwater conditions (see for example Finch and Ewing, 1992, Smith, 1983, Fayek et al, 1997, Sverjensky et al, 1992) This means that the solubility of uranium could be difficult to predict accurately in a complex environment

7.2.4 Americium

Americium is the simplest of the actinides looked at in this work as it forms only one oxidation state under natural conditions, Am(III) Other oxidation states are possible but require either very oxidizing or reducing conditions (Katz et al, 1986)

Aqueous speciation is dominated by hydrolysis reactions and carbonation It has been shown (Meinrath and Kim, 1991) that, under atmospheric conditions, hydrolysis dominates below pH 8, while at pH 8+ carbonate species are prevalent Mixed hydroxy carbonate species are also possible (Silva and Nitsche, 1995)

7.3 Solubility of actinides in cementitious environments

7.3.1 Plutonium

The solubility of plutonium under cementitious repository conditions has been measured by a limited number of workers The main problem in comparisons of solubility between workers is the crystallinity of the PuO_2 solid phase There is evidence that crystalline PuO_2 is radiolytically transformed to a new hydroxide/oxide (Berner, 1995)

Ewart et al (1992) measured Pu solubility in a Ar/H_2 atmosphere, to simulate the reducing conditions expected in a cementitious near field Figure 5 shows the resulting solubility over a pH range of 7 - 12 As can be seen the solubility of Pu is low at pHs above 8, where the aqueous concentration is below 10^{-10} M The higher solubility at lower pHs is due to the formation of Pu(III) species

Puigdomenach and Bruno (quoted in Berner, 1995) measured solubilities around 10^{-10} to 10^{-9} in the pH range from 8 to 10 Again, the solubility was seen to decrease linearly with pH below ~8 (slope ~0 9)

Measurements of plutonium solubility under aerobic conditions are more relevant to RFETS, and there are examples of these, of which only a selection is discussed here In a study aiming to deduce the effect of asphalt degradation, plutonium solubility has been measured , at pH 12, in a concrete environment (Greenfield, et al, 1997) The resulting concentration was measured as 1×10^{-10} M, in good agreement with the results of Ewart et al (1992) Allard and Rydberg (1983) discuss plutonium solubility in both aerobic and anaerobic waters over a range of pHs Under aerobic conditions, plutonium concentration is controlled by the solubility of $PuO_2(s)$, with the dominant species (in the absence of carbonate) being $Pu(OH)_4^0$ The solubility is constant between pH 5 and 10 (as Pu(III) species are less likely to form under aerobic conditions), with a concentration of 10^{-9} M

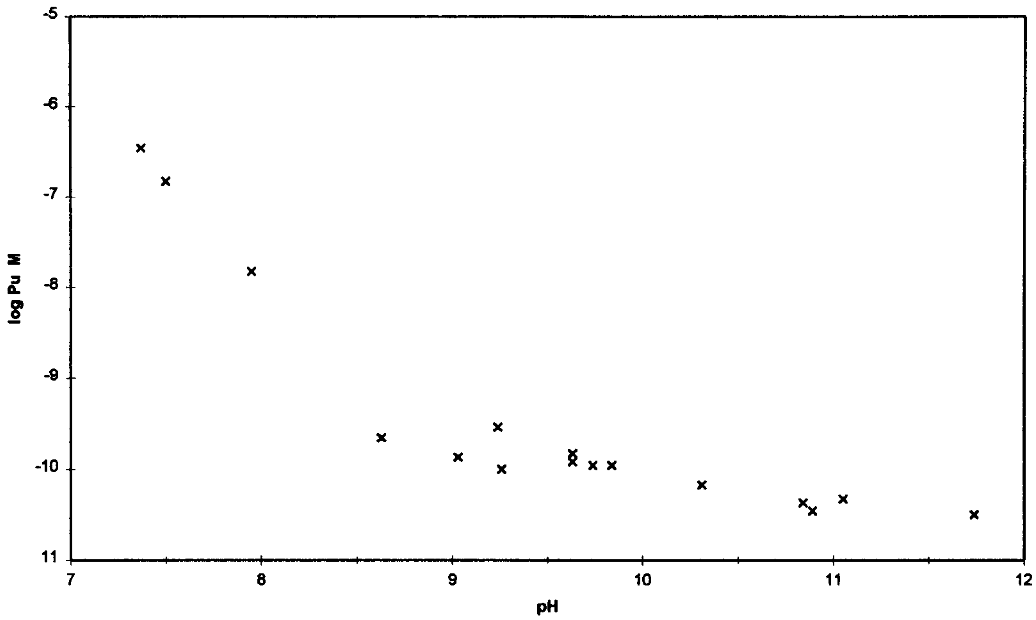

Figure 5 Measured Plutonium solubility under anaerobic conditions

In the leaching experiments described earlier (Vejmelka et al, 1991), plutonium leachability was determined to be dependent on solubility limits at pH 12 -13, and the equilibrium concentration was determined to be 1 6 × 10^{-9} M, in good agreement with the results described above

It has been discussed earlier that the impact of carbonation is likely to be significant at RFETS, and the effect on solubility needs to be assessed Kim et al (1983) observed a large increase in plutonium solubility above pH 10, in solutions containing more than 10^{-4} M carbonate Kim et al (1993) proposed that PuO_2 transforms into $Pu(OH)_2CO_3$ above pH 10, with this phase exhibiting greater solubility The basis for this assumption is the drop in aqueous carbonate concentrations, indicating formation of a carbonate phase

Yamaguchi et al (1994) also examined the effect of dissolved carbon on plutonium concentration, and they also observed increased solubility with increased carbonate levels (see Figures 6 - 7) However, Yamaguchi et al (1994) could find no evidence of carbonate uptake into a solid phase, instead they proposed that the increase in solubility is due to the formation of aqueous Pu hydroxycarbonate species The mechanism is therefore in doubt, however the increased solubility is clear, and indicated that the leaching of plutonium from concrete surfaces will be enhanced in the presence of carbonate

In conclusion, the solubility of PuO_2 is low, even under oxidizing conditions The experimental determinations range from 10^{-9} M to 10^{-10} M It must also be borne in mind that the crystallinity of the PuO_2 solid phase is a crucial factor in determining the solubility of plutonium The experiments described above used freshly precipitated or "amorphous" PuO_2 These will obviously be more soluble than crystalline PuO_2, and so the solubility limits could be viewed as maximum values However, the effect of α - decay can disrupt the crystal structure, reducing the crystallinity of the solid

In the presence of carbonate, the solubility rises seemingly linearly above bicarbonate concentrations above 10^{-4} M (at pH's below 10) and above carbonate concentrations of 10^{-3} M, above pH 12

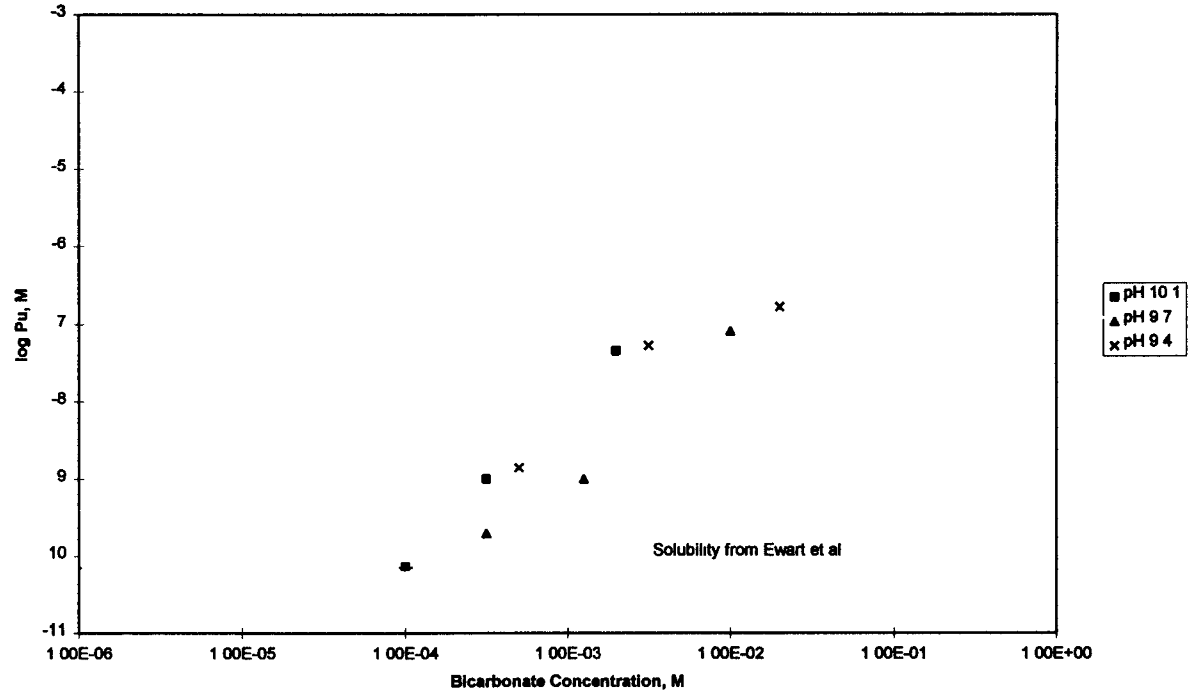

Figure 6 Plutonium Solubility as a function of carbonate concentration at pH 9 4, 9 7 and 10 1

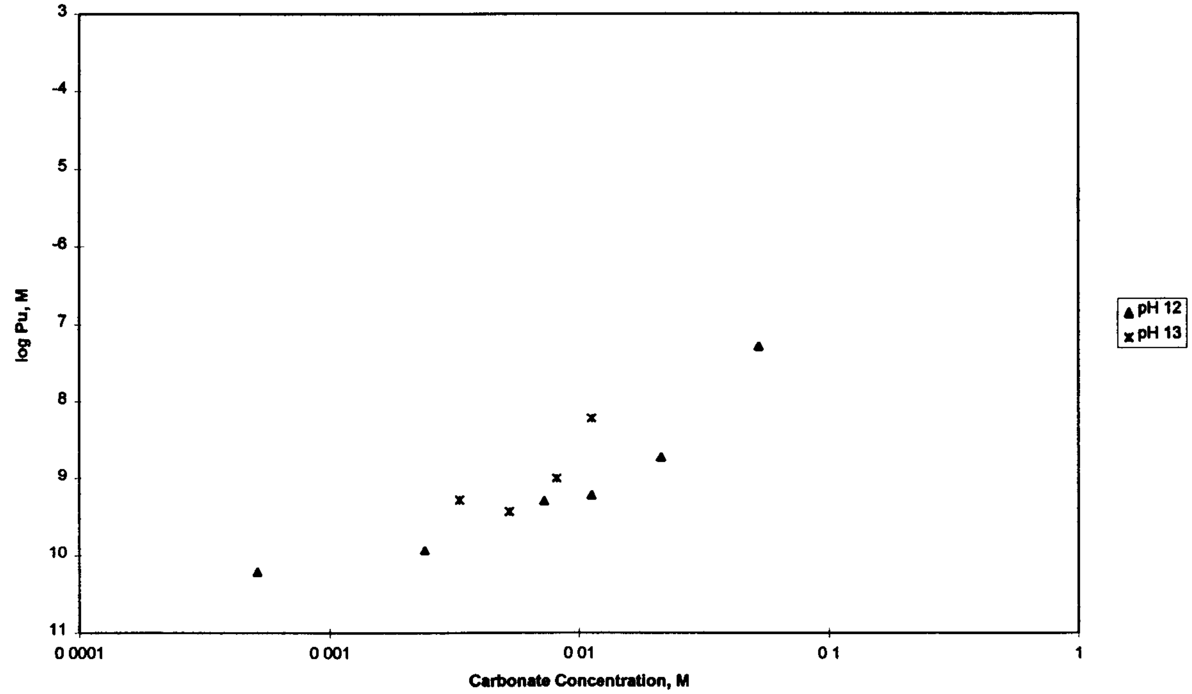

Figure 7 Plutonium Solubility as a function of carbonate concentration, at pH 12 and 13

7.3.2 Uranium

The form of uranium contamination at RFETS is not known, but may be particulate or part of the concrete aggregate, and so solubility data for uranium both in terms of UO_2 and other minerals, has been consulted The amount of available data is vast, and only a fraction is presented here, although it is hoped that the main features of uranium solubility, in a RFETS context, is preserved

The solubility of UO_2 under reducing conditions has been measured by a number of workers, and the results from two studies (Rai et al, 1990, Yajima et al, 1995) are shown in Figure 8 Both sets of experiments were carried out in inert electrolytes As can be seen, the solubility of UO_2 is defined by two distinct regions Below pH 4 - 5, uranium solubility increases with increasing pH, while from pH 5+, uranium solubility is fairly constant at 10^{-9} M (Yajima et al) and 10^{-8} M (Rai et al) A slight rise in solubility can be seen at pH's above 10 This could be due to formation of the $U(OH)_5^-$ species or partial oxidation of U(IV) to U(VI)

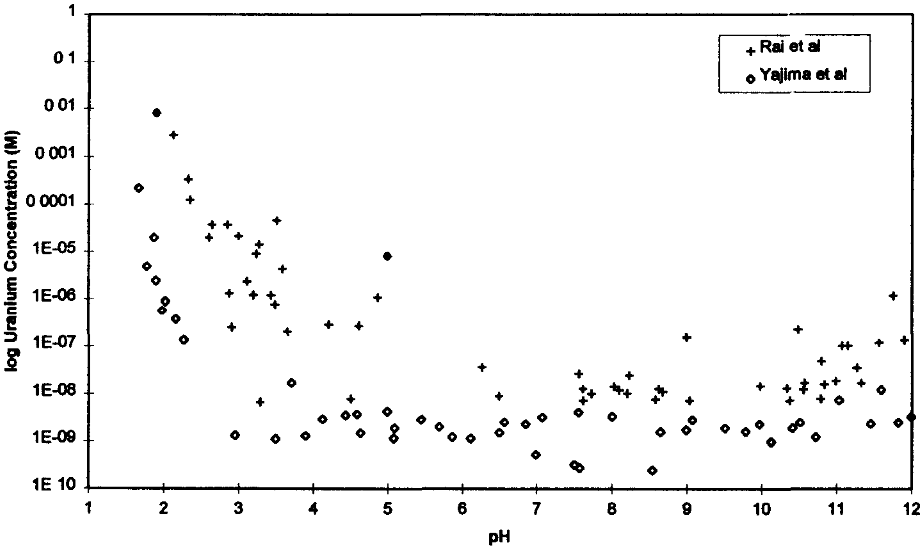

Figure 8 Measured solubility of UO_2 under reducing conditions

Similar measurements were carried out by Ewart et al (1992), over a pH range of 5 to 13, with the solution composition approximated to a 9 1 Blast Furnace Slag / Ordinary Portland Cement leachate These results showed a similar constant solubility over this pH range, although the measured aqueous concentration are significantly higher than the concentrations shown in Figure 8(3 - 2 × 10^{-7} M) There was no evidence of increasing solubility at pH 10+, in contrast to the results shown in Figure 8

The experimental evidence, therefore, seems to point to low solubilities for uranium under reducing conditions, ranging from 2 × 10^{7} to 10^{9} M, and with no alteration of the UO_2 phases These experiments are useful in that they indicate the expected uranium solubility in well defined systems However, the RFETS scenario calls for examination of uranium behavior in the presence of groundwater ions, especially carbonate and under more oxidizing conditions

If the contamination of uranium at RFETS is in the form of particulate UO_2, the mechanism of dissolution under oxidizing conditions can be complex UO_2 dissolution has been used as an analogue for the behavior of spent fuel under repository conditions, and so its behavior over a range of conditions has been examined by a number of workers (e g Casas et al, 1994, Torrero et al, 1994, Finch and Ewing, 1992, Wronkiewicz et al, 1992) A general conclusion appears to be that at least two mechanisms account for the dissolution of UO_2 under oxidizing conditions Firstly, the surface of the UO_2 is oxidized, and dissolves, releasing U(VI) into solution The second, slower mechanism involves the oxidation of the bulk UO_2, which subsequently dissolves The exact mechanism need not concern us here, but the implication is that it is the secondary minerals that control the uranium solubility under oxidizing conditions Similarly, if the source of contamination is not UO_2, these secondary minerals will be the solubility limiting phases

The most apparently simple of the uranyl (U(VI)) minerals are the uranyl hydroxides, such as schoepite, which is variously given the chemical formulae $UO_2(OH)_2$ or UO_3 $2H_2O$ It was this phase that was invoked by one of the leaching studies described earlier (Vejmelka et al, 1991) as the solubility limiting phase Schoepite exhibits the typical "U-shaped" solubility against pH behavior, with a minimum solubility around pH 7 - 8, where the aqueous concentration equals 10^{-5} to 10^{-6} M (Torrero et al, 1994) and 10^{-4} to $10^{-5.5}$M (Bruno and Sandino, 1989) The presence of carbonate, in even moderately low concentrations will tend to increase this solubility, due to the formation of uranyl carbonate aqueous species (Allard and Torstenfelt, 1985)

The presence of groundwater ions, such as carbonate, could result in the formation of other uranyl solid phases For example, Kato et al (1996b) found that the solubility limiting uranium phase under acidic conditions, with a 80% - 100% CO_2 atmosphere, is rutherfordine (UO_2CO_3), while UO_3 was the solubility limiting phase at 0 99% CO_2 atmosphere The solubility of this phase, as a function of CO_3^{2-} has recently been measured (Meinrath et al, 1996), and has been shown to be crucially dependent on the carbonate concentration, as would be expected

Cement leachates contain elevated concentrations of calcium, sodium, potassium and silica, and all of these species are capable of forming uranium solids Sandino and Grambow (1994) have shown that becquerelite (CaU_6O_{19} $11H_2O$) and compreignacite ($K_2U_6O_{19}$ $11H_2O$) are formed quickly in the presence of calcium and potassium Similarly, Brownsword et al (1990) measured uranium solubilities in sodium and calcium hydroxide solutions, and found, above pH 7, a constant solubility of 3×10^{-6} M The results did not fit the expected behavior for a schoepite type phase, and it was postulated that sodium and calcium uranates were being formed Recently, $Na_2U_2O_7$ has been identified (Yamamura et al, 1997), as has the analogous CaU_2O_7 solid phase (Heath et al, 1997) A leaching experiment described earlier (Serne et al, 1996) proposed that the observed concentrations of uranium were due to solubility limitations imposed by the $CaUO_4$ solid phase, giving aqueous concentrations of less than 10^{-8} M It must be borne in mind that no solid phase analysis was carried out, the conclusions were based solely on thermodynamic data and modelling and Berner (1992) calls into question the stability of the $CaUO_4$ in alkaline solutions

Uranium alteration by silica is a possibility in cement porewaters Finch and Ewing (1992) note that schoepite is thermodynamically unstable in waters with even low activities of calcium and silica The mineral phase, uranophane ($Ca(H_3O)_2[(UO_2)(SiO_4)]_2\ 3H_2O$) is one of the most common uranyl minerals, which may indicate that uranyl silicates are important phases controlling uranium concentrations in natural waters (Finch and Ewing, 1992) Other silicates, such as soddyite ($(UO_2)_2(SiO_4)\ 2H_2O$) may also be important The formation of uranyl solid phases within a cement matrix have recently been examined (Moroni and Glasser, 1995), with several solubility limiting phases being identified These included becquerelite, uranophane and weeksite ($K_2(UO_2)(Si_2O_5)_3\ 4H_2O$) along with several unidentified phases Uranium solubilities are reported to be around 10^{-8} to 10^{-9} M, although it should be noted that the temperature in this study was 85°C More recently, a study examining the effect of silica on schoepite transformation (Sowder et al, 1996) found no evidence of uranyl silicates being formed, even at silica concentrations of 10^{-3} M Instead, the presence of silica was seen to retard the transformation of schoepite to becquerelite in 10^{-2} M and 10^{-3} M calcium systems

Berner (1992) modelled the solubility of uranium as a function of redox conditions, through consideration of uraninite, $CaUO_4$, uranophane and "x-phase" (basically a hydrated calcium uranate) He found that under extremely reducing conditions, uraninite is the stable phase, resulting in solubilities of 10^{-8} to 10^{-10} M Under mildly reducing conditions, the solubility limiting phase depends on pH, and modelled solubilities lie between 10^{-7} to 10^{-10} M

The above discussion highlights the complexity of uranium in natural systems, and the uncertainty in knowledge of the identity of solubility controlling uranium solids under differing conditions It does appear to be evident that the presence of cement leachates does lower the solubility from the value expected from schoepite equilibrium (~10^{-5} M), whether through formation of calcium and/or silica phases The presence of carbonate, however, appears to have the opposite effect, increasing uranium solubility, either through the formation of uranyl carbonate aqueous species or uranyl carbonate phases, such as rutherfordine

7.3.3 Americium

The solubility of americium will be dominated by the formation of hydroxide, carbonate and hydroxycarbonate minerals According to Choppin et al (1995), $AmOHCO_3$ limits the solubility of americium when $[CO_3^{2-}]_{free} > 10^{-12}$ M (pH 6) and when $[CO_3^{2-}]_{free} > 10^{-8}$ M (pH 8) The number of experiments dealing with americium solubility appear to be more limited than those for uranium, and a selection of these are presented below

Atkinson et al (1988) measured americium solubility in cement equilibrated waters, between pH 8 and 13 The total carbonate concentration was 3×10^{-5} M The results showed that the solubility was equal to ~10^{-8} M at pH's below 10, falling gradually to 10^{-11} M at pH 13 The explanation given was the transformation of americium hydroxycarbonate into americium hydroxide, resulting in an inflection in the solubility curve Similar results were observed by Ewart et al (1992) also in concrete equilibrated water

The solubility of amorphous $Am(OH)_3$ in a carbonate free environment has been reported by Loida et al (1995), with the americium concentration equalling 10^{-4} M at pH 7, dropping to 10^{-9} M at pH 11 The crystallinity of the $Am(OH)_3$ is important, and Nitsche (1991) note that there is an order of magnitude difference between crystalline and amorphous $Am(OH)_3$ (e g at pH 7, solubility is $10^{-3.5}$ M for the amorphous

$Am(OH)_3$, compared to $10^{-4.5}$ for the crystalline solid) The experiments described earlier (Serne et al, 1996) showed that the leaching behavior of neodymium (an analogue for americium) was controlled by the solubility of $Nd(OH)_3$, with a solubility of 10^{-5} M at pH 7, and a solubility of below 10^{-8} M above pH 9 Assuming that the analogue between Nd and Am is a good one, this gives a good indication of americium leaching behavior in a carbonate - free environment

The effect of carbonation has been studied by a number of workers Meinrath and Kim (1991) consider the formation of $Am_2(CO_3)_3$ as the result of exposing americium to carbonated solutions The resulting solubilities range from 10^{-4} M (pH 6, carbonate 10^{-7}M) to 10^{-7} M (at pH 8, carbonate 10^{-3}M) In contrast, Nitsche (1992) found that, in trying to prepare $Am_2(CO_3)_3$, orthorhombic $AmOHCO_3$ formed in preference to $Am_2(CO_3)_3$ In addition, hexagonal $AmOHCO_3$ was found to form in Yucca Mountain groundwaters, at pH 5 9 (Nitsche, 1991) (the orthorhombic solid formed at pH 7 and 8 4) The solubilities in these Yucca Mountain groundwaters was determined to be ~10^{-8} M, with solubility rising slightly as pH is increased

Other determinations of americium solubility includes Allard and Torstenfeldt (1985), where the calculated aqueous concentration was determined to be 10^{-7} M in marl groundwater, and Vejmelka (1991), where the leachable concentration of americium was equal to the solubility limit at pH 12 -13 (2×10^{-10} M)

In conclusion, americium solubility is dependent on both pH and carbonate There is evidence of phase changes from americium carbonates, or hydroxycarbonates below pH 9, to $Am(OH)_3$ at higher pH Solubilities appear to vary from around 10^{-5} M at neutral pH's to 10^{-10} M at alkaline pH's

7.4 Sorption of actinides onto cements

Sorption data is normally presented in terms of *distribution ratios*, or R_d's (or K_d's) The distribution ratio can be easily extracted from batch sorption experiments, through use of the following expression,

$$R_d = \frac{\text{Quantity of radionuclide sorbed per unit mass of solid}}{\text{Equilibrium concentration of radionuclide in solution}}$$

$$= \left(\frac{C_1 - C_2}{C_2}\right)\frac{V}{M}$$

where C_1 = initial aqueous concentration of radionuclide

C_2 = final aqueous concentration of radionuclide

V = volume of solution

M = mass of solid phase

Cementitious materials are likely to be good sorption substrates for elements whose dominant sorption mechanism is surface complexation The specific surface area of cement materials are high, ranging from 55 to 200 m^2/g (Lea, 1980, Bradbury and Sarott, 1994), suggesting that sorption capacity is high As has been described above, the actinide elements have a significant tendency to hydrolyze, with high first hydrolysis constants (K_{11}), and high charge to bond length (z/d) ratio (Baes and Mesmer, 1986) There is a strong correlation between distribution ratios on cement, and K_{11} and z/d values (Bradbury and Sarott, 1994) It would therefore be expected that uranium, plutonium and americium would exhibit high distribution ratios

The effect of cement composition needs to be addressed Several studies (Allard et al, 1984, Allard, 1985, Atkinson et al, 1988) have suggested that the specific composition of the cement has little or no effect on the sorption of readily hydrolyzed elements, such as actinides There is evidence that the sorption of non-hydrolysed species such as Ra, Cs and I is crucially dependent on the cement composition (Heath et al, 1996, Holland and Lee, 1992, Glasser et al, 1997) In particular, the sorption of Cs (which is poorly sorbed by CSH phases) is claimed to be extremely sensitive to the composition of the ballast (aggregate) (Allard, 1985) or aluminium substitution into the cement (Glasser et al, 1997)

From the evidence, it appears that a good first approximation is that the specific cement composition has little impact on the sorption of actinides However, it must be borne in mind that most, if not all, of the experimental determinations of sorption onto cements were carried out at pH 12 and above At this pH, *and under the low carbonate levels considered*, actinides will be hydrolyzed and sorption is likely to be close to 100% Under these conditions, variations in sorption due to the composition of the cement could be masked If the porewater close to the surface of the concrete is influenced by the groundwater composition, pH will be lower than 12 and therefore, sorption may be lower and compositional variation more important

Distribution ratios gleaned from the literature do indeed show high distribution ratios for actinides on cement Below is listed a summary of some of the relevant R_d values for uranium, plutonium and americium onto cements

[illegible]	R_d (m^3/kg)	Comments	[illegible]
Uranium	0 1 - 6 3	Sorption onto seven cement blends, oxidizing conditions	Allard et al, 1984
	8	U(IV) sorption value	Heath et al, 1996
	6 2	U(VI) sorption value	Heath et al, 1996
	0 1 - 2	Recommended values for oxidizing conditions	Bradbury and Sarott, 1994
	1 - 5	Recommended values for reducing conditions	Bradbury and Sarott, 1994
Plutonium	1 2 - 12 6	Sorption onto seven cement blends, oxidizing conditions	Allard et al, 1984
	10 - 30	Variation due to variation in solid-liquid ratio	Atkinson et al, 1988
	6 6	Pu(IV)	Heath et al, 1996
	1 - 5	Recommended values for both oxidizing and reducing conditions	Bradbury and Sarott, 1994
Americium	2 5 - 25 1	Sorption onto seven cement blends, oxidizing conditions	Allard et al, 1984
	7- 60	Variation due to examination of particle size	Atkinson et al, 1988
	1 - 5	Recommended values for both oxidizing and reducing conditions	Bradbury and Sarott, 1994

Table 2 Summary of distribution ratios for actinides onto cements

Thus, the actinides, particularly americium, apparently exhibit extremely strong sorption on cementitious materials There is no apparent effect of pH, although the experiments were all carried out above pH values of ~12 5

In explaining the sorption behavior observed in these experiments, all of the authors have invoked surface complexation onto CSH phases as the most likely sorption mechanism This is likely to be true for cements that have not been extensively leached or altered by interaction with groundwaters Upon hydration, CSH forms on the outside of the cement powder particles, on the boundary between the interstitial water and the solid phases (Bradbury and Sarott, 1994) The CSH phase is almost amorphous and contains most of the microporosity of the cement Accordingly, "much of the sorption potential associated with cement arises from the CSH micropore network and its concomitant high surface area" (Glasser, 1992)

However, the situation is likely to be different for a cement that has been leached, or more relevant to RFETS, carbonated Carbonation results in the formation of calcium carbonate, which tends to fill space (and block cracks), and form a relatively dense skin of solids, effectively isolating the cement phases from the aqueous phase (Glasser et al, 1997) This means that calcium carbonate solids will become the dominant sorption substrate, with a resultant drop in sorption For example, Stenhouse (1995) reports R_d values of 0 02 m^3/kg, 0 4 - 5 m^3/kg and 5 m^3/kg for uranium, plutonium and americium sorption on calcite These distribution ratios are significantly lower than corresponding cement R_d's, particularly for uranium

The precipitation of calcium carbonate minerals at the cement surface may induce the formation of co-precipitates with the actinide elements already present Co-precipitation of trace elements within a calcium carbonate solid phase is a well investigated phenomenon (e g Comans and Middelburg, 1987), with strontium predicted to be particularly effected (Plummer and Busenberg, 1987) An important consequence of co-precipitation is that, in contrast to surface sorption, the contaminant is held irreversibly, and so is inaccessible to the aqueous phase This obviously has important consequences for the leaching of radionuclides from the surface of buried concrete, and therefore needs to be assessed

Carllsson and Aalto (1996) have recently examined the co-precipitation of uranium with calcium carbonate The results indicated that, under the experimental conditions (pH 9 6 and 8 5, in both nitrogen and CO_2 atmosphere) uranium did not co-precipitate with calcium carbonate It was postulated that dominant species in solution, uranyl carbonates, were not of suitable size and charge to be incorporated into the calcite structure This result confirmed earlier work by Carroll and Bruno (1991) who showed that co-precipitation did not occur over the range of experimental conditions

In contrast to these experimental results, recent modelling work (Curti, 1998) predicts that the trivalent and tetravalent actinides will be significantly affected by co-precipitation with secondary calcium carbonate minerals The implication to the behavior of Pu(IV) and Am at RFETS is clear However, this work must be viewed with caution The results presented are purely the result of modelling, based on a simple distribution law model This in itself is not reason to be cautious However, the important parameter, the partition coefficient, has been estimated from consideration of the solubility products of pure metal carbonates, R_d values and the ionic radii of the metals It is not clear at this point as to the validity of this approach, and experimental confirmation is required The study does, however, emphasize the potential effect of calcite co-precipitation, and could be an important mechanism in the determination of leaching behavior at RFETS

The conclusion from this survey of sorption processes is that actinides are strongly sorbed onto cement phases, with americium particularly strongly sorbed It would therefore seem that if uranium, plutonium and americium were sorbed onto the surface of concrete the concentration released into the aqueous phase will be limited However, the surface of a buried concrete structure will be extremely susceptible to groundwater influences, particularly carbonation Carbonation produces precipitates of calcium carbonate, for which the actinides have a lower affinity, resulting in less retention Co-precipitation, which would effectively retard the release of contamination irreversibly, does not appear to be a viable mechanism for uranium, and, although a theoretical study has demonstrated the possible consequences for plutonium and americium, further experimental work is needed before firm conclusions can be made

8. Summary and Conclusions

A literature search and review has been undertaken regarding the processes controlling the behavior of plutonium, uranium and americium in contaminated concrete at RFETS The review has concentrated on two aspects degradation of the concrete surface layer, where the bulk of the contamination exists, and a review of experimental studies of leaching of plutonium, uranium and americium from cement-based materials It was quickly apparent that there was a significant lack of data on the latter Consequently literature on radionuclide solubility and sorption have been examined to provide a background understanding of the behavior of actinides in cementitious environments

8.1 Concrete Degradation

A review has been carried out on literature concerning the long-term degradation of cement and concrete used in radioactive waste encapsulation, and in repository structural designs, together with more general literature on the surface-dominated degradation of concrete and cement The findings of this review have been considered together with site specific geochemical data to understand the likely behavior of the surface layers of contaminated concrete, where the majority of the contamination exists

The main form of concrete degradation occurring in RFETS concrete is likely to be carbonation of the surface During this process carbon dioxide present in air, soil gas and dissolved in groundwater reacts with calcium phases ($Ca(OH)_2$ and CSH) within the cement matrix to produce calcium carbonate and silica Supporting evidence for this process comes from experimental studies, and examination of ancient analogues of modern OPC concrete From modelling studies and examination of long-term carbonation it is likely that carbonation of the concrete surface will extend to a depth of around 10cm in the 1,000 year period considered and will thus include the zone of contamination of plutonium, uranium and americium resulting from nitrate solution and particulates

Since the background groundwater at RFETS is dilute other forms of concrete degradation such as sulfate and chloride attack are unlikely to be effective In the industrial area of the site significant sulfate concentrations are measured (1000 mg/l) at which the ettringite form of sulfate promoted attack might be expected if these sulfate concentrations were maintained in the vicinity of the disposed concrete

Other degradation processes to consider are the corrosion and expansion of steel rebars, which will produce cracking of large blocks of concrete, corrosion will occur at maximum rate since corrosion protection offered by the high pH of unleached concrete will not be effective in close contact with groundwater Microbial induced degradation of concrete has been considered, particularly since the contamination is located at the concrete surface where microbial growth is most likely There is however no clear evidence that microbial activity will be significant, although substrates for microbial growth are present at RFETS (e g pyrite, sulfate)

Degradation by carbonation is unlikely to disrupt the mechanical structure of the surface layers of concrete since the calcium carbonate formed is an effective cement which has been shown to survive for 2,000 years in ancient structures Porosity is also reduced by carbonation that will reduce the effect of purely physical degradation processes such as freeze-thaw Freeze-thaw and mechanical erosion of the concrete surface will be effective given the seasonal climatic variation and the topography at RFETS, such factors will also depend on the nature of disposal such as depth of burial Gross breakdown of concrete blocks is most unlikely over a period of 1000 years and thus access to uranium contamination in aggregate by groundwater will be restricted Growth of carbonate could conceivably entrap particulate contamination in the surface layer and restrict access by groundwater Degradation by sulfate attack or microbial action is more likely to dissaggregate the surface layers of concrete and is likely to provide better access of groundwater to contamination Plutonium, uranium and americium contamination could be mobilized from the surface of concrete by colloidal material generated from concrete degradation The most likely colloids formed from degradation of RFETS concrete are silica colloids resulting from carbonation of CSH phases and iron hydroxide colloids formed from steel corrosion Studies of colloid formation in cement leachate has been examined in carbonate free experiments, however these are not applicable to RFETS as the CSH colloids produced are unlikely to be stable in the presence of carbon dioxide The ability of colloids to significantly increase radionuclide mobility in cementitious system has been brought into question recently

Chemical degradation of cement and concrete is critical to the mobility of plutonium, uranium and americium In addition to changes in cement mineralogy chemical degradation controls the composition of the local fluid which influences actinide solubility and sorption pH redox potential (Eh) and carbonate content are all important factors controlling solubility and sorption The most significant effect of concrete degradation is a reduction in pH from over 12 in fresh cement pore fluid containing free alkalis to pH~10 5 buffered by CSH phases and finally to a pH ~8 buffered by carbonate phases The aqueous carbonate content is controlled by CO_2 partial pressure that is influenced by external controls such as plant and microbial respiration in the soil zone and exchange with the atmosphere Cement and concrete will also regulate the CO_2 partial pressure in a closed system Degradation of the cement matrix is unlikely to influence Eh, however corrosion of steel rebars is likely to produce anaerobic conditions

Overall, from information in the literature it is possible to qualitatively predict the degradation behavior of concrete at RFETS to provide background information for evaluating the chemical controls on leaching, solubility and sorption of plutonium, uranium and americium Some areas of uncertainty that have arisen during this review are

- Consideration of the effect of sulfate contamination in groundwater in the industrial area, is it representative of long-term composition?

- The potential role of microbiological processes in influencing concrete degradation and in controlling redox conditions
- The potential for generation of actinide sorbing colloids during carbonation of concrete

The lack of understanding of processes of redox control and colloid transport are uncertainties which are not necessarily confined to this study but are significant to radionuclide mobility in general at RFETS

8.2 Leaching, solubility and sorption of plutonium, uranium and americium in cementitious systems

Experimental measurements of the leaching of plutonium, uranium and americium from cement matrices are very limited in extent The main reason appears to be the low mobility of actinides in cementitious environments, with a consequent need for long time scale experiments Literature on radionuclide solubility and sorption have been consulted, to provide an understanding of the likely behavior of actinides in a cementitious environment From the results of this literature review, the following conclusions can be made

Firstly, the penetration of uranium, americium and plutonium into intact concrete is very low, even when the radionuclides are in aqueous solution This confirms the supposition that any concrete contamination at RFETS will be surficial In addition, the low diffusivity means that any uranium present in the concrete aggregate should not leach into the groundwater, in significant quantities, over a 1,000 year time scale

The diffusion coefficients presented by two sets of workers are reasonably consistent, especially so when the low mobility and thus difficulty in measurement is taken into account The diffusion coefficient for plutonium was determined to be 2×10^{-17} m^2/s (Albinsson et al 1993) and 1×10^{-16} m^2/s (Vejmelka et al, 1991) For americium, the corresponding D_a's are 0 3 - 1 8 $\times 10^{-17}$ m^2/s (Albinsson et al, 1993) and 2×10^{-17} m^2/s (Vejmelka et al, 1991)

The mechanisms controlling radionuclide leaching from cement or concrete are sorption onto the cement matrix and precipitation of solid phases The dominant mechanism will depend on the initial concentration of the radionuclide In general, radionuclides below the solubility limit will exhibit a linear increase in leached concentration, as sorption dominates (assuming linear sorption) Above a certain concentration, solubility limits will determine the leached concentrations, this value will correspond to the maximum extent of leaching, and will be fixed, unless geochemical conditions change

The immediate environment of the concrete will be characterized by high pH, with the leachate containing elevated concentrations of calcium, silica and, initially at least, alkalis, such as Na and K In addition, carbonation is likely to occur, inducing calcite precipitation All of these factors, as well as the composition of the groundwater are likely to influence the leaching behavior of the actinides

The solubility of plutonium, uranium and americium, over a range of conditions, have been examined In general, solubility is expected to be low at high pH's and low carbonate Plutonium, for example, is likely to have a solubility between 10^{-9} M and 10^{-10} M The effect of carbonation is likely to be crucial, with plutonium exhibiting increased solubility when bicarbonate concentrations are above 10^{-4} M Uranium and americium are likely to change phases as a result of carbonation The effect of calcium, silica and potassium on uranium solubility has been examined, with the conclusion that formation of phases such as uranophane will tend to reduce solubility The formation of these phases under site specific circumstances, however, will have to demonstrated There is lack of data on similar phases of americium and plutonium, should they exist

Sorption of actinides onto cements is likely to be high, as would be expected by easily hydrolyzed elements, and R_d values are as high as 30 m^3/kg All of the measured R_d 's have, however, been measured at very high pH's (12 - 13), which is more akin to the environment of cement - encapsulated waste It is not clear whether these conditions will apply to the immediate environment of surface contaminated actinides In particular, carbonation will result in the precipitation of calcite, which will present a new sorption substrate to the radionuclides Sorption onto calcite appears to be less strong than sorption onto cement phases The possibility of irreversible, co-precipitation of the actinides with calcite has to be considered The experimental data suggests that co-precipitation of uranium (VI) with calcite does not occur, probably due to the size and charge of the uranyl carbonate aqueous species However, it has been shown, theoretically, that co-precipitation could have a major impact on radionuclide migration

From this literature review, it is clear that there are a number of dominant factors that will influence the leaching of radionuclide - contaminated concrete A preliminary list of these factors is listed below,

I Nature of contamination - this will determine the penetration of the radionuclide into the concrete (i e aqueous contamination will penetrate more deeply), and the initial solid phase present

II The amount of contamination - different mechanisms (sorption or solubility) will operate at different concentrations If the contamination is predominantly surficial, it is more difficult to define a g/g concentration

III Geochemical Conditions - the conditions in the immediate environment of the contamination is crucial in the determination of leach behavior e g

- A interaction of the groundwater with the concrete and concrete porewaters
- B pH and pe - the mobility of radionuclides in any environment is crucially dependent on these two parameters
- C ligands - e g carbonate, calcium, alkalis, sulfate, and organics
- D alteration of cement minerals - co-precipitation
- E nature of solubility limiting phase, if any

In summary, it is likely that the leaching behavior of uranium, plutonium and americium, on purely chemical considerations, is controlled, ultimately, by the equilibrium with a solubility controlling solid phase The exact nature of this solid phase, and the value for its solubility limit will be complex, and will depend on all the factors mentioned above

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11. Appendix B

Appendix B: Calculation of Actinide Solubility Limits

1. Introduction

This section details the determination of solubility limits for plutonium, uranium and americium under cementitious environments Two scenarios are considered

1 Solubility corresponding to fresh cement ($Ca(OH)_2$)
2 Solubility corresponding to carbonated cement (calcite as main solid phase)

The geochemical code PHREEQC (Parkhurst, 1995) was used, in conjunction with thermodynamic data from the HATCHES version 9 database (HATCHES, 1996)

2. Results

2.1 $Ca(OH)_2$

The solubility of the three radionuclides in equilibrium with $Ca(OH)_2$ are shown in Table 1

Radionuclide	Solubility limiting phase	pH	[illegible]
Pu	$Pu(OH)_4$	12 5	$7\,4 \times 10^{-11}$
Pu	PuO_2 (c)	12 5	$1\,2 \times 10^{-18}$
Am	$Am(OH)_3$	12 5	$5\,7 \times 10^{-11}$
U	CaU_2O_7	12 5	$1\,2 \times 10^{-6}$
U	$CaUO_4$	12 5	$4\,2 \times 10^{-14}$
U	$UO_3\,2H_2O$	12 4	$1\,5 \times 10^{-2}$

Table 1 Calculated solubilities in equilibrium with $Ca(OH)_2$

To calculate an activity from these concentrations, the following expression is used

$$\mathrm{Activity}(\mathrm{Ci}/\mathrm{l}) = \frac{c \times N_A \times \lambda}{3\,7 \times 10^{10}}$$

where

c = concentration (moles / l)

N_A = Avogadro's number

λ = decay constant (s^{-1})

$1Bq = 3\,7 \times 10^{10}$

with the decay constants given by

Pu-239	$9\ 110 \times 10^{-13}\ s^{-1}$
Pu-240	$3\ 347 \times 10^{-12}\ s^{-1}$
Pu-241	$1\ 525 \times 10^{-9}\ s^{-1}$
Am-241	$5\ 074 \times 10^{-11}\ s^{-1}$
U-234	$8\ 939 \times 10^{-14}\ s^{-1}$
U-235	$3\ 121 \times 10^{-17}\ s^{-1}$
U-238	$4\ 916 \times 10^{-18}\ s^{-1}$

The isotopic composition was taken from the Rocky Flats Cleanup agreement (DOE, 1996), and are shown in Table 2 The crucial influence of the solubility limiting solid can clearly be seen, when the calculated activities are compared with the MCL's for plutonium and americium in groundwater In fact, only the solubilities corresponding to PuO_2 and $CaUO_4$ appear to be below the appropriate levels

[illegible]	[illegible]	[illegible]	[illegible]
Pu	$Pu(OH)_4$	93 8% Pu-239, 5 8% Pu-240, 0 36% Pu-241	7663
Pu	PuO_2 (c)	93 8% Pu-239, 5 8% Pu-240, 0 36% Pu-241	0 07
Am	$Am(OH)_3$	100% Am-241	47080
U	CaU_2O_7	100% U-238 100% U-235 100% U-234	96 610 1746149
U	$CaUO_4$	100% U-238 100% U-235 100% U-234	$3\ 36 \times 10^{-6}$ $2\ 13 \times 10^{-5}$ 0 061115

Table 2 Calculated activities at solubility limits

2.2 Calcite Environment

PHREEQC calculations were undertaken to determine the solubility of uranium, plutonium and americium under calcite equilibrated solutions This was done because the groundwaters at Rocky Flats appear to be in equilibrium with calcite, and so the immediate environment on the surface of any buried concrete is likely to be characterized by precipitation of calcite The pH was varied to account for uncertainties in the composition of the water in contact with the contaminated concrete

Figure 1 shows the calculated solubility of plutonium, from pH 7 to pH 10, with calcite equilibrium maintained Figures 2 and 3 show the results of equivalent calculations for americium and uranium respectively The solubility of all three radionuclides drops dramatically as pH drops, and carbonate increases (the carbonate levels in equilibrium with calcite are of the order of mM concentrations)

3. Solubility limits with relation to Concrete contamination

From Table 1 and Figures 1 - 3, it is possible to calculate the extent of contamination on the concrete surface that will lead to a solubility-limited system This type of calculation will help to more efficiently design experimental leaching experiments For example, if an experiment is set up such that a 60mm diameter concrete disc contaminated with americium is in contact with 100ml of calcium carbonate saturated groundwater at pH 8, the contamination needed to be at the solubility limit can be calculated thus

1 From Figure 2, the solubility of americium is approximately 10^{-6} moles/l -> 10^{-8} moles/100ml,
2 The surface area of the concrete disc $= \pi r^2$,
$= 2827$ mm^2 (0 003 m^2),
3 Thus, to be above the solubility limit, americium must be present at 10^{-8} moles/0 003m^2,
$= 3\ 3 \times 10^{-6}$ moles/m^2,
$= 101\ 9$ MBq/m^2 or $101\ 9$ Bq/mm^2
$= 0\ 002$ Ci/m^2

Thus, if the concentration of americium is above $3\ 3 \times 10^{-6}$ moles/m^2, in this experiment, the leaching behavior will be controlled by the solubility of the relevant solid phase, in this case $Am_2(CO_3)_3$

4. Conclusions

The calculations shown here show that the solubility limits for uranium, plutonium and americium are above the tolerated activities for Rocky Flats The exception is if crystalline PuO_2 is the solubility controlling solid phase It is uncertain at this point whether the contamination on the surface of Rocky Flats concrete is in the form of highly crystalline plutonium dioxide, or whether a more amorphous form is prevalent

The calculations indicate that, if the contamination is present at levels such that the distribution is solubility controlled, the resulting contamination leached to the groundwater will be too high to comply with Rocky Flats Action Levels

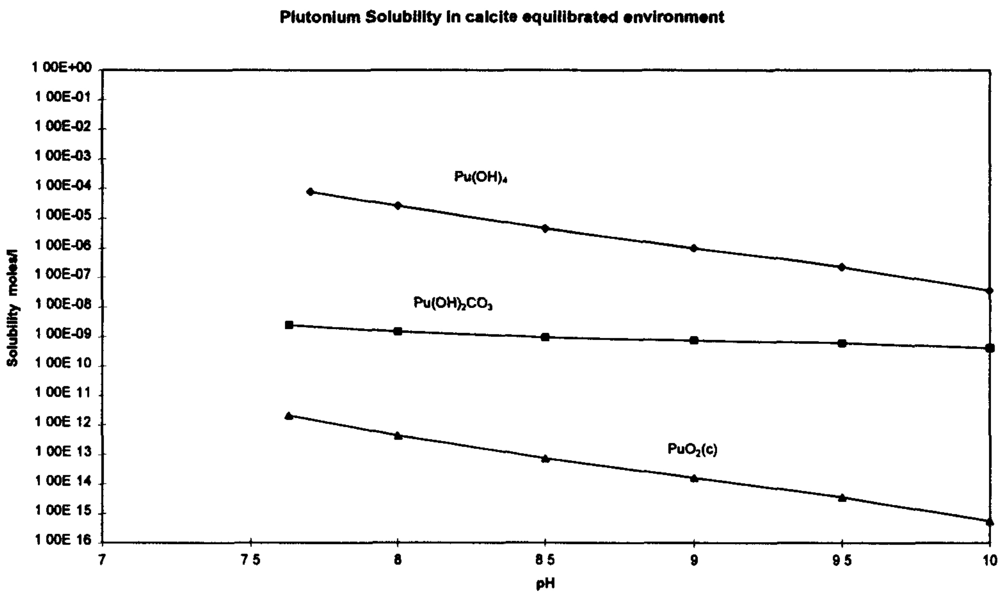

Figure 1 Calculated plutonium solubility in a calcite equilibrated environment

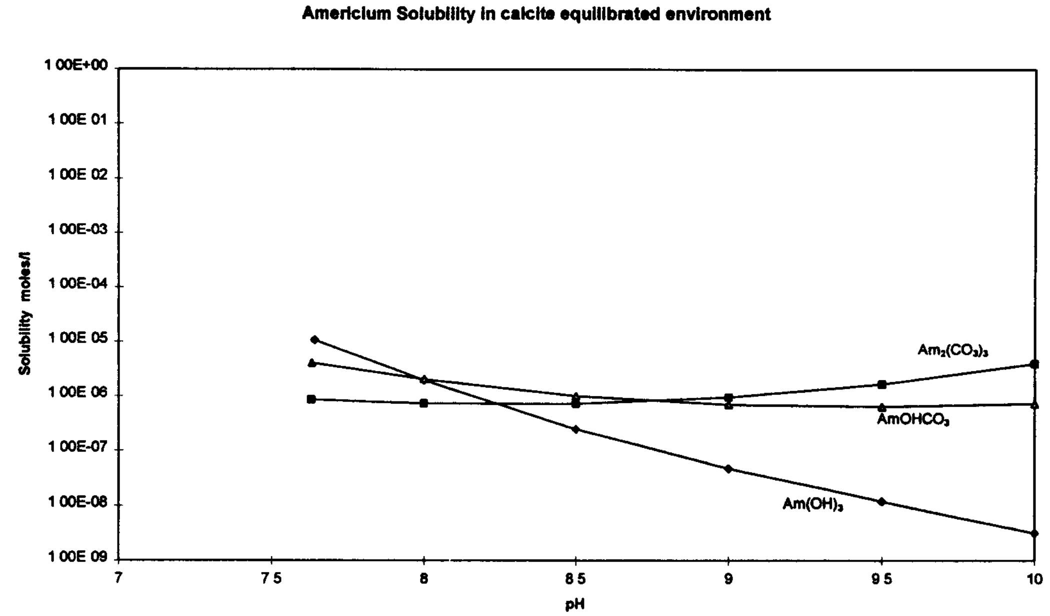

Figure 2 Calculated americium solubility in a calcite equilibrated environment

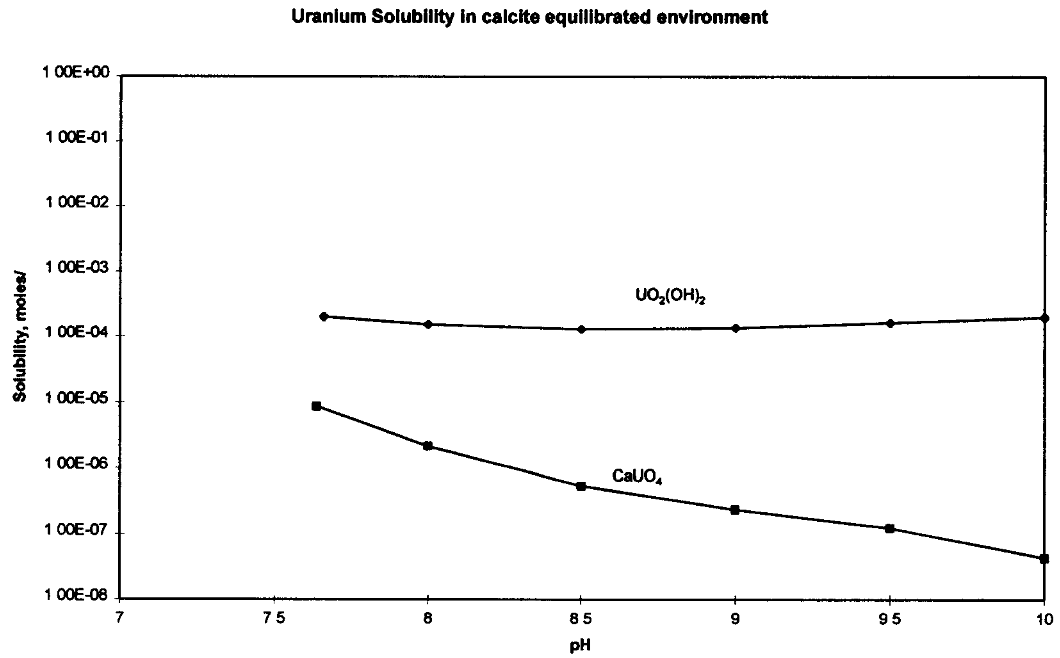

Figure 3 Calculated uranium solubility in a calcite equilibrated environment

$AmOHCO_3$	-5 7
$Am(OH)_3$	15 4
$Am_2(CO_3)_3$	-33 4
PuO_2	-7 4
$Pu(OH)_4$	0 4
$Pu(OH)_2CO_3$	-25
CaU_2O_7	42
$CaUO_4$	24 94

Table 3 Thermodynamic Data for solid phases used in geochemical calculations

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